Review of biochar role as additive in anaerobic digestion processes

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Abstract

Anaerobic digestion (AD) could be considered as a mature technology and nowadays it can still play a pivot role because of the urgent need to provide renewable energy sources and efficiently manage the continuously growing amount of organic waste. Biochar (BC) is an extremely versatile material, which could be produced by carbonization of organic materials, including biomass and wastes, consistently with Circular Economy principles, and "tailor-made" for specific applications. The potential BC role as additive in the control of the many well-known critical issues of AD processes has been increasingly

explored over the past few years. However, a clear and comprehensive understanding of the connections between BC and AD is still missing. This review paper analyses and discusses significant references (review articles, research papers and international databases and reports), mostly published in the last 10 years. This review is aimed at addressing three key issues related to the better understanding of the BC role in AD processes: 1. Investigation of the influence of BC properties on AD performances and of their ability to counteract its main challenges; 2. Assessment of the optimal BC production chain (i.e. feedstock-pyrolysis-activation) to achieve the desired features; 3. Evaluation of the economic and environmental advantages connected to BC use in AD processes, compared to conventional solutions applied to address AD challenges.

Highlights

- Biochar key properties were specific surface, pores and surface functional groups
- Lignocellulosic biomass, slow pyrolysis and physical activation made the best biochar
- Biochar addition exhibited economic and environmental advantages
- Biochar improved methane production (in average 25 %) and digestate quality

Keywords: anaerobic digestion; biochar; bioenergy; biomass; circular economy; waste

Abbreviations

AD: anaerobic digestion; BC: biochar; BET: Brunauer–Emmett–Teller; CE: circular economy; CEC: cationic exchange capacity; CIC: controlling internal circulation; CLSM: confocal laser scanning microscopy; COD: chemical oxygen demand; DIET: direct interspecies electron transfer; EAC: electron accepting capacity; EDC: electron donating capacity; EU: European union; FAN: free ammonia nitrogen; FISH: Fluorescence in situ

hybridization; FW: food waste; GAC: granular activated carbon; GHG: green-house gas; HRT: hydraulic retention time; IET: interspecies electron transfer; LCA: life cycle analysis; MSW: municipal solid waste; OFMSW: organic fraction of municipal solid waste; OLR: organic loading rate; PAH: polyaromatic hydrocarbons; PCBs: polychlorinated biphenyls; S/I: substrate to inoculum ratio; SMP: specific methane potential; SS: suspended solids; SSA: specific surface area; TAN: total ammonia nitrogen; TPAD: two phased anaerobic digestion; TSS: total suspended solids; UASB: up-flow anaerobic sludge blanket; VFA: volatile fatty acids; WAS: waste activated sludge; WWTP: wastewater treatment plant; WV: working volume; V: volume.

Contents

1. Introduction

The global energy consumption increased from around 8,800 million tonnes of oil equivalents (Mtoe, including coal, gas, oil, electricity, heat and biomass) in 1990 to 14,400 Mtoe in 2018 [1]. In 2016 renewable energy sources met this demand for about 14 % of primary energy supply, while fossil fuels accounted for 81% of greenhouse gas (GHG) emissions [2]. The need to decrease fossil fuel dependency and GHG emissions and to generate economic benefits is stimulating initiatives to produce energy as well as high-value chemicals and products from sustainable non-food biomass, residues, co-products and wastes.

Anaerobic digestion (AD) is a well-established technology for the treatment of wastewater and organic waste, e.g. the organic fraction of the municipal solid waste (OFMSW), waste activated sludge (WAS), animal manure, etc. Biogas can directly replace fossil fuels in heat and power generation or be upgraded to bio-methane as vehicle fuel or injected in the gas grid [3], while digestate can be employed as soil amendment [4,5]. Other benefits of AD, compared to alternative treatment options applied to organic waste, include control of odor and GHG emissions, removal of pathogens and adaptability to many substrates [6]. AD has been extensively implemented, from small-scale applications, particularly in rural areas and developing countries, to large-scale industrial plants [7]. Despite the rapidly growing number of biogas installations in Europe (from about 6,200 to 18,202 between 2009 and 2018) [8], many challenges regarding AD processes still persist. Different options have been explored to address these challenges: optimization of working parameters and bio-reactor configuration, co-digestion and nutrients control [9]; adoption of pre-treatments to enhance the degradability of various substrates [10,11]; use of inorganic and biological additives to support biomass

immobilization, supplement nutrients, mitigate inhibitors and improve process stability [12–14].

Among the additives, conductive carbonaceous materials, as granular activated carbon (GAC) and biochar (BC), gained interest because of their ability of enhancing methane production [15,16]. BC may present several advantages over other additives; it can be produced with a wide variety of physico-chemical properties by controlling feedstock, pyrolysis operating conditions and the activation process [17,18], resulting "tailor-made" for specific applications. In recent years, several authors confirmed the possibility of increasing methane production through BC addition (Table 1), suggesting different potential mechanisms: (1) increase of the buffering capacity of the AD system; (2) mitigation of inhibition phenomena or agents; (3) support media for biomass immobilization; (4) promotion of syntrophic metabolisms; (5) enhancement of digestate quality; (6) biogas cleaning and upgrading. The most significant and updated scientific literature investigating the BC role within AD processes can be classified as follows (Table 1):

- Studies considering the advantages of coupling AD with thermal processes (gasification, pyrolysis and hydrothermal carbonization) from a general point of view;
- Studies exploring the positive influence of BC on AD, based on methane and/or biogas production enhancement and/or improvement of digestate quality;
- Studies analysing in detail the BC features that may influence one or more of the above-mentioned mechanisms.

Considering the digestate, BC has been reported to enhance its quality in terms of nutrient retention, increase of the carbon-to-nitrogen ratio and reduction of nutrient leaching [19].

129 Consequently, BC doesn't need to be separated from digestate at the end of its utilization

130 in AD.

131

132 Table 1. Overview of literature studies exploring the connections between BC and AD

Studies considering the general advantages of coupling AD with thermal processes	Studies exploring the positive influence of BC on AD, based on a general analysis of methane and/or biogas production enhancement	Studies exploring the positive influence of BC on AD, based on a general analysis of the improvement of digestate quality	Studies analysing in details the biochar features that may influence one or more of the six above-mentioned mechanisms
Pecchi and Baratieri, 2019 [20] Fabbri and Torri, 2016 [21] Hübner and Mumme, 2015 [22] Salman et al., 2017 [23]	Linville et al., 2017 [24] Torri and Fabbri, 2014 [25] Sunyoto et al., 2016 [26] Jang et al., 2018 [27] Sun et al., 2019 [28] Zhao et al., 2015 [29] Inthapanya et al., 2012 [30] Inthapanya and Preston, 2013 [31]	Bruun et al., 2011 [32] Shen et al., 2016 [33] Shen et al., 2017 [34]	Fagbohungbe et al., 2017 [19] Ye et al., 2018 [13] González et al., 2018 [15] Zhang et al., 2018 [16] Codignole Luz et al., 2018 [35] Masebinu et al., 2019 [36] Pelaez-Samaniego et al., 2018 [37] G. Wang et al., 2018b [38] D. Wang et al., 2017 [39] Fagbohungbe et al., 2016 [40] Mumme et al., 2014 [41] Shanmugam et al., 2018 [42] Su et al., 2019 [43] Lü et al., 2016 [44] Cruz Viggi et al., 2017 [45] Li et al., 2018 [46] Martínez et al., 2018 [47] Luo et al., 2015 [48] Wang et al., 2019 [49] C. Wang et al., 2018 [50] Zhao et al., 2016 [51] Yu et al., 1999 [52] Cooney et al., 2016 [53] Dang et al., 2017 [54] Sasaki et al., 2010 [55] Martins et al., 2018 [56] S. Chen et al., 2014 [57] Pan et al., 2019b [58] Qiu et al., 2019 [59]

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135 To the best of our knowledge, despite the growing number of studies investigating the
136 connections between BC and AD, three main issues still need to be explored: a clear
137 comprehension of the above-mentioned six mechanisms; a correlation between BC
138 features and their effects on AD processes; environmental and economic outcomes related
139 to BC use. The present review is therefore aimed at addressing the following issues: 1)
140 investigation of the influence of BC properties on AD performance and of their ability to
141 counteract its main challenges; 2) assessment of the optimal BC production chain (i.e.
142 feedstock-pyrolysis-activation) to achieve the desired features; 3) evaluation of the
143 economic and environmental advantages connected to BC use in AD processes, compared
144 to conventional solutions applied to address AD challenges.

145 **2. Review methodology**

146 The selection of scientific literature was made considering the following criteria:
147 a) *Relevant international databases and information sources*. Bibliometric sources as
148 Web of Science, Science Direct and Scopus were used to retrieve articles, book-chapters
149 and proceedings of indexed conferences. Official international databases (Eurostat,
150 International Energy Agency, European Biogas Association, etc.) were searched for the
151 selection of technical reports and statistics;
152 b) *Chronological order*. The majority of the references in this review are from 2015 to
153 2019 (67 %) and from 2009 to 2014 (26 %), with the balance before 2009 (7 %);
154 c) *Relevant keywords for the topics of interest*. A first survey adopted the following
155 keywords in different combinations: “biochar, anaerobic digestion, methane, pyrolysis,
156 economic assessment, environmental assessment, life cycle analysis, LCA”. Based on

157 this preliminary selection, the review questions have been identified. Thereby, additional
158 keywords have been adopted to face specific issues, as: “biochar, buffer capacity,
159 anaerobic digestion, volatile fatty acids”, “biochar, ammonia inhibition, ammonia
160 removal, anaerobic digestion”, “syntrophic metabolisms, biomass immobilization,
161 biochar, anaerobic digestion, DIET, electron transfer”.

162 d) *Selection of the references based on content analysis.* After a first screening
163 considering the abstracts of all identified reference sources, 259 relevant references
164 were analyzed as full content and included in this review. The relevant scientific
165 content was sourced from scientific articles (240 research papers and reviews – 93 %),
166 book chapters and indexed conference proceedings (11 documents – 4 %), and
167 international databases and reports (8 documents – 3 %). Considering only the
168 scientific research papers and the reviews, they were related to (Figure 1): AD (31 %)
169 and pyrolysis (10 %); coupling AD and thermal processes (10 %); BC features (25 %);
170 BC and AD interaction mechanisms (14 %); economic and environmental aspects
171 related to BC use (10 %). The distribution of the relative contributes of the scientific
172 literature to the different topics concerning the investigation of BC role in AD in 2009
173 – 2019 exhibits a clear increasing trend due to a growing interest, particularly in the
174 last five years, for the topics covered by the present work and consequently strengthens
175 the need to address the above mentioned review questions.

176 This review is structured according to the contents outline. At the end of each section, the
177 last paragraph summarizes the main findings and research gaps of the specific topic
178 explored, which are finally condensed in the conclusions.

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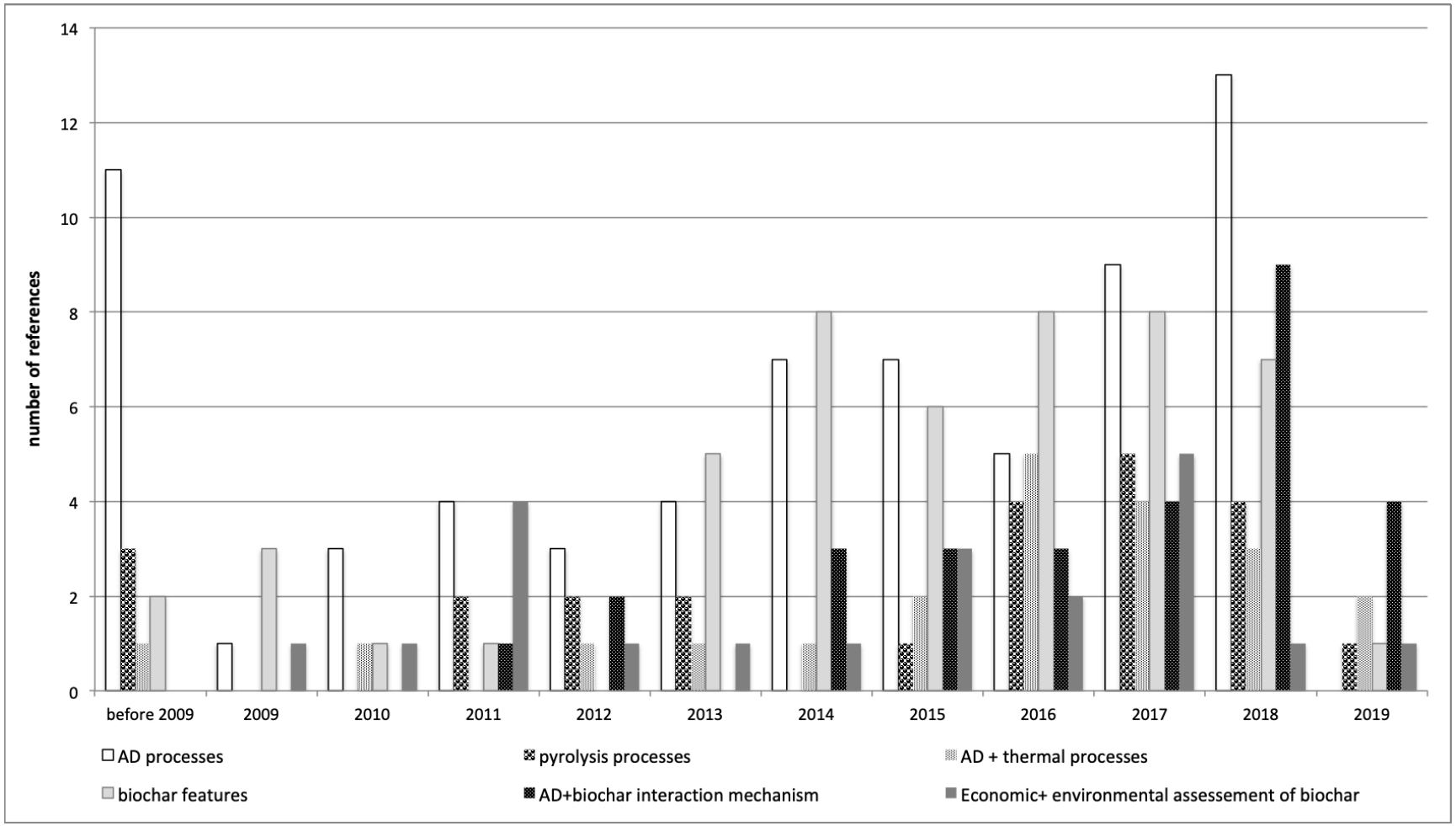
180 Figure 1. Relative contributions of the scientific literature selected for this work



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3. Biochar

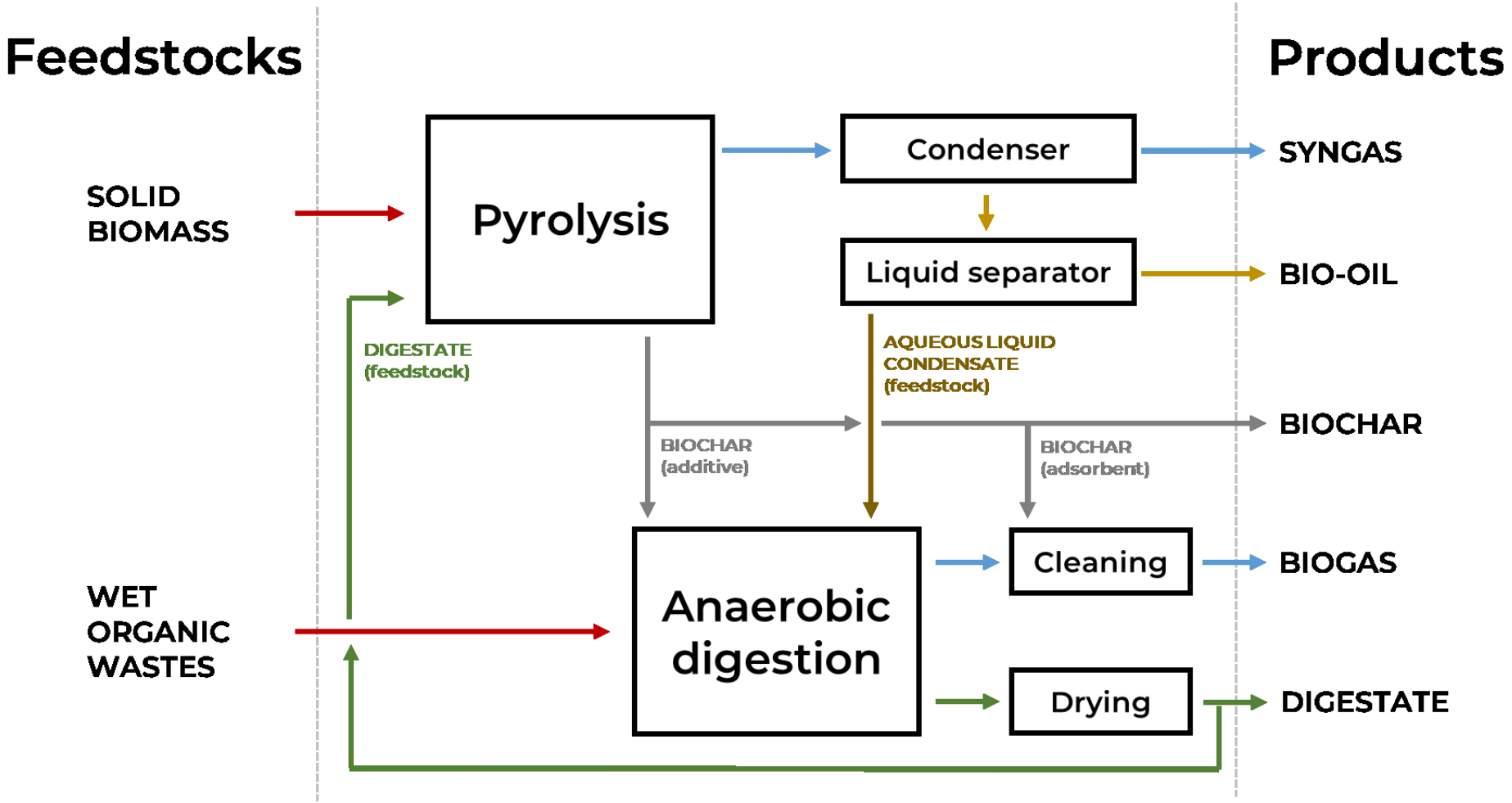
BC is the porous carbonaceous solid residue of the complex physical and chemical phenomena simultaneously occurring during the thermochemical treatment of raw biomass [60–63]. While AD is particularly suitable to produce biogas and digestate from wet organic waste (Figure 2), pyrolysis is a thermochemical process able to convert solid dry biomass in an oxygen-limited environment into valuable liquid chemicals (bio-oil), as well as gaseous biofuels and charcoal (biochar, BC) [64–67]. Although pyrolysis was conventionally mostly focusing on the production of liquid biofuels from woods and purpose-grown energy crops, the most recent studies found that it is not cost effective unless the feedstock is inexpensive, dry and readily available, and there are valuable chemical co-products (liquid bio-oil and solid BC) or favorable government policies [68]. Both AD and pyrolysis can contribute to fulfill Circular Economy targets, but research on biological and thermochemical processes traditionally progressed along parallel and separate pathways, often in competition.

In recent years, improved understanding of the characteristics of bio-oil and BC has helped to develop key quality requirements to expand their potential value [69]. High value liquid bio-oil products can be obtained from the pyrolysis of biomass residues, such as phenolic substitutes for adhesives or antioxidants [70,71]. However, there are limitations: the most valuable chemicals are usually mixed with impurities that impair their properties. Similarly, there are many promising applications for BC, such as soil improver [18], composite materials [72], activated carbon [73], electrodes for batteries or electrolysis cells [74], metallurgical coke substitute [75], catalyst for tars [76], and could be eligible for carbon credits [77]. The efficiency of BC in most applications significantly

depends on its physico-chemical properties and elemental composition, which are subject to variations depending on feedstock, pyrolysis conditions, pre- and post-processing treatments.

The characteristics of AD and pyrolysis processes and products may offer interesting opportunities for the integration of such technologies (Figure 2), with the objective of contributing to the Circular Economy. For example, pyrolysis could be utilized to convert dewatered digestate into BC, which could then be used for a variety of applications [17,78,79], including its potential use to improve the quality of biogas and digestate [37], or to reduce instabilities and inhibition in digestors [16,24]. On the other hand, the acetic acid-rich aqueous pyrolysis condensate could be utilized as a feedstock for AD, possibly with the addition of BC for the selective adsorption of toxic inhibitors [21–23,25,80–88]. In conclusion, BC represents the key link between pyrolysis and AD and, consequently, in this section we wish to review its characteristics, including suitable feedstocks, production technologies, activation processes and characterization techniques.

221 Figure 2. Outline of potential integrations between anaerobic digestion and pyrolysis (derived from [20,21]).



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3.1. Feedstocks

During thermal processing under oxygen free or oxygen-limited conditions (as pyrolysis), as the temperature increases, the polymeric components of lignocellulosic biomass crack and liquid intermediate phases are formed with different visco-elastic behaviors [89,90]; under slow progressive heating, cellulose remains hard and elastic up to 400 °C, whereas hemicellulose softens within a relatively narrow temperature range (230 to 280 °C) and remains viscous, while lignin softens and bubbles over a broader temperature range (150 to 350 °C) and remains mainly elastic. The overall process cannot be simply designed based on the linear combination of the behaviors of the individual components, but it is the result of their interactions at different temperatures and it is catalyzed by the mineral matter present in the ashes. As the temperature increases over these ranges, the depolymerized liquid undergoes two competitive processes, oligomer evaporation and crosslinking reactions, with the former favored at high heating rates, and the latter under slow pyrolysis. These findings explain why, under slow pyrolysis, the char yield is greater, and the particles globally keep the same macro-structure of the original biomass, although forming an intermediate soft material. Montoya et al. (2017) [91] confirmed the presence of molten liquid intermediates formed from cellulose, xylan and lignin and showed that the presence of minerals prevents the complete liquefaction of the xylan, therefore contributing to the preservation of the general shape and structure of the solid material during pyrolysis.

Therefore, BC can be produced from a wide range of lignocellulosic materials, containing cellulose, hemicellulose (xylan), lignin, small quantities of other organic compounds (phenols, phytosterols and fats) and inorganics (P, N, S, Si, alkali and alkaline earth metals and traces of other minerals). Such materials include wood, agricultural and forest

residues, food waste, sugars, industrial organics, sewage sludge and manure. BC can be mesoporous or microporous depending on the operating conditions employed for its production and on the feedstock.

3.2. Thermochemical production

Recent reviews illustrated the different technologies and processes used experimentally and industrially to produce BC [17,92]. These include torrefaction, pyrolysis, gasification, combustion and hydrothermal carbonization [93]. Scale and potential mobility are important considerations in relation to the feedstock supply, logistics, seasonality, further refining, of products quantities, characteristics and value, and potential markets [17,60].

Torrefaction involves biomass treatment at atmospheric pressure and within a temperature range of 200–300 °C, without oxygen or with limited oxygen supplies [94]. As discussed earlier, partial depolymerization and liquefaction of the biomass components take place reducing the biomass tenacity and improving grindability. Torrefaction produces char with less moisture, higher energy density, lower weight, lower O/C and H/C ratio, increased hydrophobic nature and resistance to biological degradation with respect to the original feedstock. Typical yields of torrefied biomass range between 50 and 80 % [95].

Gasification is a thermochemical process carried out at temperatures higher than 750 °C in the presence of a gasifying agent (air, oxygen, or steam) at atmospheric or at high pressures. Under these conditions, biochar yields are not sufficiently significant to consider gasification an appropriate BC production process. Similarly, combustion is not a suitable BC production process, since, under good combustion conditions, BC yield should be negligible.

272 The various modes of *pyrolysis* include slow, intermediate, fast, flash, and ultra-pyrolysis,
273 carried out under vacuum, atmospheric pressure or under pressure [65,69]. As a result of
274 the balance between primary, secondary cracking and recombination reactions, bio-oil
275 yields are typically maximized (up to 70 %) at intermediate temperatures (450-550 °C),
276 faster heating rates (100-500 °C/s) and short vapor residence times (< 1~2 s), which are
277 characteristic of fast and flash pyrolysis. Under these conditions, BC yields are typically
278 of the order of 15~20 %. On the other hand, higher BC yields (25~40 %) are achieved at
279 moderate temperatures (300-450 °C), slower heating rates (~ 1 °C/s) and longer vapor
280 residence times (> 5~10 s), representative of slow or intermediate pyrolysis, when bio-oil
281 yields vary between 40 and 50 % with the balance being gas.
282 *Hydrothermal carbonization (HTC)* is performed on wet biomass (moisture > 10 %) as
283 feedstock, making the process highly energy-intensive [96]. HTC happens under water in
284 a sealed confined system and heated at the temperature range of 175–300 °C for up to 16
285 h under saturated pressure under subcritical conditions producing tar-free BC (hydrochar)
286 with large number of functional groups [97–99]. Hydrochars are usually obtained at
287 yields of 20-25 % [96], and they contain mainly aliphatic compounds and more oxygen
288 functional groups and higher cation exchange capacity than conventional BC. On the
289 other hand, they have lower surface area, microporosity and carbon stability [96,100].
290 Among the various thermal technologies, pyrolysis has been the most investigated
291 technique and it is considered the best technology for the production of BC [101] from
292 relatively dry feedstock (moisture content below 10 %). However, also HTC is gaining
293 interest to produce hydrochar, particularly from wet biomass [96]. In a comparison
294 between the chars, it should be noticed that BC yields are higher, as well as porous
295 structure and aromatics and ash contents, while hydrochar exhibits a non-porous

296 structure, lower fixed and total carbon contents and higher amounts of alkyl functional
297 groups [96].

298 *3.3. Activation*

299 BC with different properties can be produced from a wide range of feedstock and by
300 adjusting processing conditions. Further modification of BC chemical and physical
301 properties can be achieved through a process defined "activation", aimed at increasing
302 BC porosity and modifying its pore size distribution (Figure 3), as well as to some extent
303 surface chemistry. Activation can be carried out in a number of ways, depending on type
304 of activation agents (e.g. physical and chemical activation) or mode of operation into
305 single-stage or multi-stage activation.

306 *Chemical activation* utilizes chemical agents, e.g., H_3PO_4, HNO_3, KOH, NaOH, H_2SO_4,
307 and $ZnCl_2$ [102,103]. It typically involves two steps; in the first the feedstock is
308 impregnated with a selected chemical agent, and then thermally treated in the second step.
309 Another option is the activation of already produced BC by soaking it in a chemical agent,
310 followed by a thermal treatment. Depending on the agent selected and thermal treatment
311 conditions used, different degrees of activation can be achieved. The activated BC needs
312 to be thoroughly washed with deionized water to neutralize its pH and to remove any
313 remaining chemicals [104], and this procedure can contribute to a negative environmental
314 impact of the technology. Oxidative activation that uses acidic or alkaline agents is among
315 the most common activation methods. Besides enhancing porosity and surface area, it
316 also creates oxygen-containing functional groups on the surface of BC (e.g. carboxyl,
317 hydroxyl, lactone, phenol, carbonyl, and peroxide groups). These functional groups play
318 an essential role in different applications of BC, such as for contaminant removal or
319 nutrient sorption.

320 *Physical activation* does not utilize chemicals, thus avoiding some of the negative
321 environmental impacts that can be associated with chemical activation. Instead, BC is
322 exposed to physical oxidizing agents, such as steam, CO_2, ozone or air/O_2, typically at
323 temperatures above 700 °C. These gaseous agents penetrate the internal structure of BC
324 gasifying the carbon atoms, which results in opening and widening of pores [105].
325 Similarly to chemical activation, physical activation not only enhances BC porosity, but
326 also modifies its surface functional groups, increasing the abundance of oxygen
327 functional groups [105].
328 In conclusion, both chemical and physical agents can be used effectively to activate BC
329 and obtain high porosity, surface areas over 1000 m^2/g, and modified surface functional
330 groups, tuned to specific applications. The key challenges of BC activation are without
331 any doubt related to their potential negative environmental impacts, mainly for chemical
332 activations, and high-energy intensity need.

333 *3.4. Physico-chemical characteristics*

334 The variability of BC physico-chemical properties resulting from the proper selection of
335 feedstock, pyrolysis and activation can be adapted to a wide range of applications.
336 S*pecific surface area* (SSA), expressed as m^2g^{-1}, is the ratio between the total surface area
337 and the total particle mass of BC [106], commonly determined by Brunauer–Emmett–
338 Teller (BET) analysis. The reported SSA values of BC can vary significantly, in the range
339 10^0 - 10^2 m^2g^{-1} [107,108] depending on pyrolysis temperature and feedstock, and up to
340 over 10^3 m^2g^{-1} after activation. SSA is a key parameter enhancing the adsorption capacity
341 of BC, even if the chemical composition of its surface is determinant in the interactions
342 with other species [109]. SSA is related to BC pore size distribution [18].

343 P*orosity* can be described by the pore volume (m^3g^{-1}) and by the pore size distribution,
344 including micro-, meso-, and macro-pores (respectively < 2nm, 2-50 nm, >50 nm) [110],
345 based on their internal diameters. The relative abundance of these pores produces
346 different BC structures (Figure 3), since micro-pores have the major contribute to BC
347 surface area, micro- and meso-pores are essential for its adsorption capacity, while macro-
348 pores can provide an appropriate habitat for microorganisms [18,111]. Yin et al. (2017)
349 [112] stated that within a proper range, a high temperature results in a large surface area
350 and pore formations. Trigo et al. (2016) [113] found that SSA increased between 350°C
351 and 700 °C for different hardwood biochars, while Chen et al. (2014) [114] revealed an
352 enhanced porous structure of BC from sewer sludge varying the temperature from 500 °C
353 to 900 °C.
354 Specifically considering the effect of the feedstock on BC characteristics [101], yields
355 and aromatic functional groups are much higher from lignin (48.8 %) than from
356 hemicellulose (21.1 %), while no differences were found in the elemental composition of
357 resulting BCs. High lignin and mineral content in the feedstock result in higher yields of
358 BC [115,116]. Woody and grassy biomasses generate a more carbon-rich BC when
359 compared to sewage sludge and manure [32,117,118]. Specifically considering the effect
360 of pyrolysis process on BC characteristics [119], increasing pyrolysis temperature
361 decreased concentrations of aliphatic carbons, oxygenated functional groups, nitrogen,
362 oxygen and hydrogen. However, carbon mass fraction, micropore volume, ash content,
363 fixed carbon and carbon stability increase with higher pyrolysis temperatures.
364

365 Figure 3. SEM micrographs of (A) raw biomass (eucalyptus) and of derived (B) biochar and (C) physically activated biochar (Courtesy of
366 the authors. The samples were produced at ICFAR and analysed at Politecnico di Torino).

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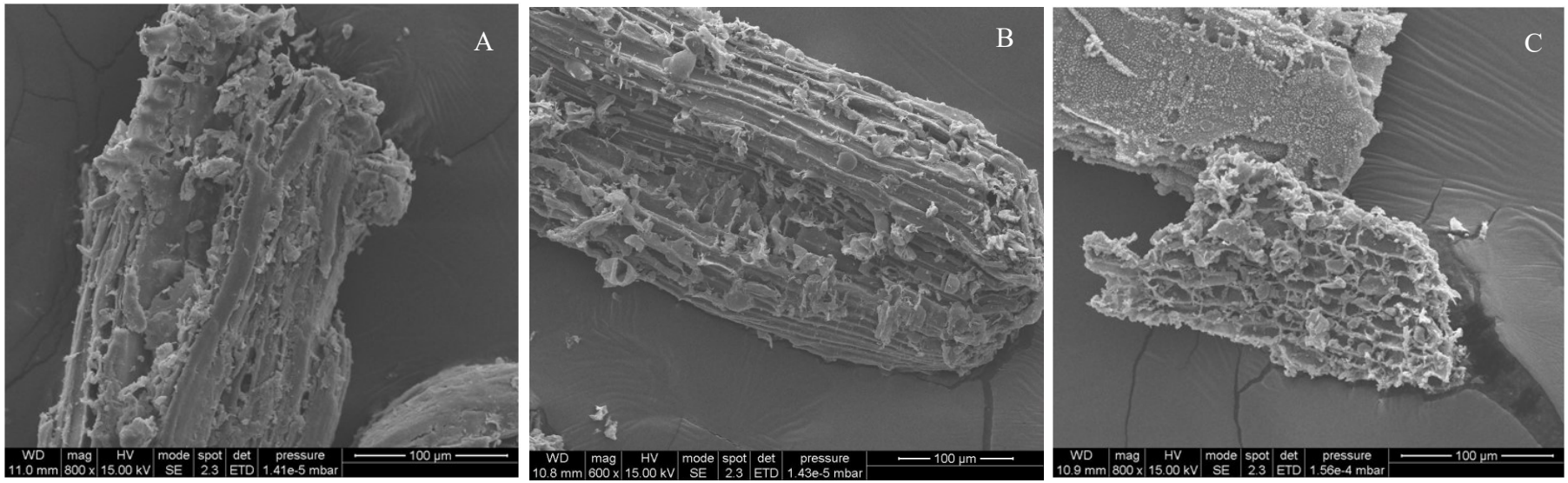

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377 BC *composition* is mainly of C, H, O, N, and S, along with mineral trace components,
378 such as K, Ca and Mg, varying according to pyrolysis conditions and feedstock [110].
379 The mineral content can be enhanced by increasing the temperature of pyrolysis [107].
380 The *cationic exchange capacity* (CEC) of BC can be defined as its ability of absorbing
381 and attracting cations (nutrients and heavy metals) decreasing with higher pyrolysis
382 temperature [18]. A high CEC value is due to a negative surface charge of BC. The
383 presence of *surface functional groups* such as hydroxyl, carboxylic, and amino, expressed
384 respectively as atomic ratio of H/C, O/C, and N/C (generally studied by Fourier transform
385 infrared (FTIR) spectroscopy), mostly depends on the feedstock and it is reduced with a
386 higher temperature of pyrolysis [107]. Further, the H/C ratio is considered as a measure
387 of the degree of aromatization of BC and the O/C ratio as an indication of more
388 oxygenated functional groups, contributing to high CEC values and hydrophilicity of BC
389 [120,121]. An increase in pyrolysis temperature has been reported to negatively affect the
390 amount of acidic functional groups and the CEC [112,122].
391 *pH values* are generally basic and increase as the pyrolysis temperature grows, due to the
392 volatilization of acidic functional groups and to the higher ash content [18]. Moreover,
393 BC can present redox characteristics, being able to donate and accept electrons, and these
394 tendencies are quantified respectively by the *electron donating* and *accepting capacities*
395 [110]. Phenolic groups may be the electron donating species, while quinones and
396 polycondensed aromatic structures the electron accepting compounds [110,123]. In
397 addition, the *electrical conductivity*, expressed as S m^{-1}, decrease as consequence of the
398 increase of the pyrolysis temperature [17].
399 A full characterization of BC involves several analytical methods [124]. Scanning
400 electron microscopy (SEM) is employed to investigate the superficial structure of BC, as

401 well as its chemical composition if coupled with energy dispersive X-ray spectroscopy
402 (SEM-EDX); transmission electron microscopy (TEM) allows to observe BC bulk
403 structure; X-ray diffraction (XRD) analysis detects the crystalline phases; nuclear
404 magnetic resonance (NMR) spectroscopy investigates BC composition, specifically the
405 aromatic structure; X-ray photoelectron spectroscopy (XPS) quantitatively analyses the
406 superficial composition.

407 **4. Application of biochar as additive in anaerobic digestion**

408 *4.1. Buffer capacity and alkalinity*

409 The volatile fatty acids (VFAs) produced as intermediates during AD tend to lower the
410 pH [125]. This effect is generally counteracted by syntrophic acetogens and methanogens
411 microorganisms, which convert VFAs to methane and carbon dioxide [126]. However, in
412 case of high organic loads of easily biodegradable wastes (i.e. when the VFAs production
413 rate exceeds the consumption rate), the accumulation of VFAs can occur, resulting in pH
414 drop and even in the failure of AD [126,127]. The buffer capacity in a digestor is linked
415 to the ability to neutralize VFAs, and it is considered a rate-limiting step in AD processes
416 [38,39,128]. The buffer capacity is determined by the alkalinity of the AD system, mainly
417 in the form of carbon dioxide and bicarbonate [6,125]. So it is technologically challenging
418 to build a bioreactor aimed at digesting easily biodegradable feedstock with high pH
419 buffer capacity [16]. Even if several methods have been proposed (Table 2) so far, the
420 most diffused solution to improve buffer capacity implemented both at lab [129] and full
421 scale [130] is co-digestion. In particular, manure or sewage sludge showed high buffer
422 capacity, mainly due to the quite high ammonia content, which is able to counteract the

423 pH drop due to VFAs production. Therefore, manure or sewage sludge are often co-
424 digested with OFMSW and/or agricultural waste biomass.

425

426 Table 2. Advantages and disadvantages of conventional methods for creating buffering
427 capacity in bioreactors

Methods	Advantages	Disadvantages
Alkaline pretreatment [131]	Cellulose more available to the enzymes	Expensive and considered as the technological bottleneck
Commercial alkaline materials (e.g. NaOH and $CaCO_3$) [132,133]	Easy pH adjustment	pH continually should be analyzed Temporary Lower biogas output at higher organic loads
Co-digestion [16]	Increasing methane yield Low cost and green	Hard to achieve an appropriate mixture of feedstocks to limit VFAs production
Geopolymer (Composite and monolith) [132,133]	Controllable alkali leaching Prevent the need for continuous pH adjustment	25 g L^{-1} costs around 0.10 $

428

429 However, it still remains a great challenge to develop simple, permanent and cost-
430 effective methods to improve buffer capacity of AD systems. Nowadays, BC is
431 considered as an attractive alternative to the aforementioned methods for two important
432 reasons. Firstly, it can be produced via cost-effective and environmentally friendly
433 approaches. Secondly, its physical and chemical properties can be matched with the
434 operational conditions [19,40,41].

435 BC's buffer capacity mainly depends on two factors:

436 I. *Functional groups*: Rapid accumulation of VFAs during AD process results in a
437 medium with low pH value in which some functional groups of BC like amine
438 adsorbs H^+ and accepts electron. This phenomenon could mitigate the sudden pH
439 drop.

II. *Inorganic materials*: Ash portion of biochar contains inorganic materials such as Ca, K, Mg, Na, Al, Fe, Si and S. Among them, alkali and alkaline earth metals (AAEMs) are responsible for alkalinity of biochar via reaction 1 (Ca and CxHxCOOH are selected as representative of AAEMs and VFAs, respectively) [16]:

$$CaCO_3 + 2C_xH_xCOOH \rightarrow [C_xH_xCOO]2Ca + H_2O + CO_2 \quad (1)$$

Table 3 shows the literature data related to BC buffering capacity and its effects on bio-methane production, showing total alkalinity, pH values and the increase in CH_4 production (%), ranging from 8 % up to about 26 %. Some studies suggest that the alkalinity of BC due to AAEMs in ash fraction could effectively contribute to the buffering capacity of AD against VFAs inhibition. Jang et al. (2018) [27] investigated the effects of BC from dairy manure on AD of dry dairy manure at 20°C, 35°C, and 55°C. In each case they observed a lower total VFAs concentration and increased methane production. They suggested the role of high nutrients (9.1% Ca, 3.6% Mg, 1.3% N, 0.14% P) and alkalinity potential of BC in enhancing methane production. Wang et al. (2017) [39] investigated the role of BC from vermicompost on the buffering capacity of AD of high organic loads of kitchen waste and chicken manure. The authors proved the high buffer capacity of vermicompost BC to different short-chain VFAs (700-3800 mg L^{-1}), probably due to the presence of AAEMs and superficial functional groups. Linville et al. (2017) [24] studied the effects of BC from walnut shell during the AD of FW in mesophilic and thermophilic conditions. They observed that BC improved process stability by enhancing the total alkalinity from 2800 to 4800-6800 mg L^{-1} $CaCO_3$ and pH (initial pH >8) in BC amended digesters. Wei et al. (2020) [134] found enhanced methane production and solids removal by adding BC from corn stover (rich of alkaline earth metals) to AD of primary sludge. The authors observed higher total alkalinity (3500-4700

464 mg L^{-1} $CaCO_3$) and pH in BC amended reactors, suggesting that BC provided a strong
465 buffering capacity. Ambaye et al. (2020) [135] investigated the role of BC from sewage
466 sludge on the AD of fruit waste. They observed that the BC addition enhanced methane
467 production and VFAs degradation. Further, the deficiency of some nutrients or trace
468 elements in the substrate may cause an increase of VFAs inducing inhibition of microbial
469 activity during AD [33,135]. Extra doses of trace metals may be required for an effective
470 activity of methanogens without VFAs accumulation [136]. Thereby, it could be
471 speculated that BC could provide adequate concentrations of trace metals for the stability
472 of the AD system [135].
473 In summary, BC addition can counteract VFAs inhibition in case of high loads of easy
474 degradable wastes such as FW, OFMSW, primary sludge. The alkaline nature of BC
475 determining its pH buffering capacity may contribute to prevent VFAs inhibition. The
476 ash fraction of BC contains AAEMs possibly contributing to its acid-buffering capacity
477 and important trace elements for microorganisms. However, further investigations are
478 required to confirm the effectiveness of these mechanisms and to identify the optimal
479 dose of BC related to these properties. Higher doses can be toxic for AD [24,134], perhaps
480 due to inhibitory concentrations of alkali metals [137]. Besides, other mechanisms could
481 be responsible of BC role in alleviating VFAs inhibition. Porous BC could provide
482 support for biofilm growth and protection to selectively enriched functional microbes
483 closely attached to it under acid stress [48]. Secondly, BC could promote the activity of
484 microbial partners enhancing the syntrophic VFAs degradation and methane production
485 under high organic loads [38,138]. The latter microbial mechanisms will be fully adressed
486 in section 4.3.
487

488 Table 3. Results of pH drop and CH_4 production/yield of AD processes in the presence
489 of various types of BCs

Pyrolysis Operational condition				**AD Operational conditions**				**Results of buffering effect**					**Ref**
Temp (C°)	Time (min)	Reactor	Feedstock	Temp (C°)	HRTor duration (d)	Substrate	inoculum	Total alkalinity (g L^{-1} $CaCO_3$)		pH		Increase in CH_4 (%)	
								Control	BC	Control	BC		
350	180	Muffle furnace	dairy manure	20	35	dairy manure	Anaerobic sludge	1.8-4.8	5.3-7.3	7.18	7.71	26.47[a]	[27]
350	180	Muffle furnace	dairy manure	35	35	dairy manure	Anaerobic sludge	1.8-4.8	5.3-7.3	7.09	7.68	24.90[a]	[27]
350	180	Muffle furnace	dairy manure	55	35	dairy manure	Anaerobic sludge	1.8-4.8	5.3-7.3	7.12	7.55	24.69[a]	[27]
500	120	Tube furnace	vermi-compost	35	50	chicken manure	Anaerobic sludge	6.0	7.3	7.0-7.1	7.8-8.0	N.P.	[39]
500	120	Tube furnace	vermi-compost	35	50	kitchen waste	Anaerobic sludge	0.0	2.3	3.5-3.7	4.7-4.9	N.P.	[39]
600	120	Kiln	corn stover	55	15	primary sludge	Anaerobic sludge	2.8	3.5-4.7	7.2	7.6-8.0	8.6-17.8[a]	[134]
350	15		sewage sludge digestate	37		fruit waste	Anerobic sludge	N.P.	N.P.	4.5-5	7-8	13-27[a]	[135]
550	15		sewage sludge digestate	37		fruit waste	Anerobic sludge	N.P.	N.P.	4.5-5.5	7-8.6	12-22[a]	[135]
500	120	Slow pyrolysis	rice straw	35	25	Municipal solid waste	Anaerobic sludge			7.8	7.5	11.69[a]	[139]

a) **CH_4 Yield; N.P: Not provided**.

490
491
492 *4.2. Adsorption of inhibitors*

493 Inhibition is often defined as the predominant cause of reduction of bio-methane yields
494 and instability of AD processes. A substance can be identified as "inhibitor" when it
495 determines an adverse shift in the microbial population or arrests of the bacterial growth
496 [137]. There are direct inhibitors, such as metals (Cu^{2+}, Zn^{2+}, Cr^{3+}, Cd, Ni, Pb^{4+}, Hg^{2+},
497 Na^{+}, K^{+}, Mg^{2+}, Ca^{2+}, Al^{3+}), organic compounds (chlorophenols, halogenated aliphatics,
498 pesticides, antibiotics, lignocellulose hydrolysate); and indirect inhibitors, such as VFAs,
499 long-chain fatty acids, hydrogen, ammonium and sulphides [19]. Among the inhibitors,
500 ammonia (NH_3 or free ammonia nitrogen, FAN) and ammonium (NH_4^{+}) concentrations
501 are considered crucial (ammonia and ammonium are together considered as total
502 ammonia nitrogen, TAN). The optimal control of ammonia and ammonium may ensure
503 stable bacterial growth and significantly contribute to the buffer capacity of the AD

504 system. However, excess FAN/TAN concentrations are major causes of AD failure
505 [140,141]. Chen et al. (2008) [137] reported a wide range of TAN concentrations
506 (between 1.7 and 14 g L^{-1}) causing a 50 % reduction in methane production. FAN
507 concentration is considered the main cause of inhibitions for methanogens [140,142] and
508 it was reported to have a toxic effect to anaerobes ranging from 150 to 1200 mg L^{-1}
509 [143,144]. Various mitigation strategies have been investigated to effectively counteract
510 TAN/FAN inhibitory effects on AD. Some were based on the removal and
511 immobilization of the inhibitor, as: dilution, co-digestion and microbial adaptation [145–
512 147]; struvite precipitation [148]; use of a microbial desalinisation cell [149]; ammonia
513 stripping [150]. An alternative approach is based on the use of adsorbents, inorganic as
514 zeolites [142] and organic as GAC [143] and BC [41].
515 Based on several studies focusing on BC impacts on AD and ammonia inhibition (Table
516 4), it seems that BC could effectively mitigate ammonia inhibition, resulting in reduced
517 lag phase and enhanced methane production respect to control reactors. Some authors
518 [33,34,151] promoted BC use in AD of sewer sludge. Mumme et al. (2014) [41] revealed
519 that BC from pyrolysis of paper sludge and wheat husks could limit mild ammonia
520 inhibition (2.1 g TAN kg-1). Su et al. (2019) [43] stated that the addition of BC may
521 alleviate inhibition in case of up to 1500 mg L^{-1} ammonia-N in food waste AD [152]. Lü
522 et al. (2016) [44] revealed that BC can support AD under high ammonium stress (up to 7
523 g-N L^{-1}). The above-mentioned studies suggest a positive effect of BC towards ammonia
524 inhibition, however, there isn't full agreement on the mitigation mechanisms
525 hypothesized: cation exchange capacity [34,151]; chemical and/or physical adsorption
526 capacity and surface functional groups [33,34,151]; promotion of direct interspecies
527 electron transfer (DIET) [44,153]; immobilization of microorganisms [43,44].

528 Therefore, BC may contribute to ammonia mitigation by direct (cation exchange capacity,
529 adsorption, surface functionality) and/or indirect factors (DIET and immobilization of
530 microorganisms), depending on the characteristics of both BC and digested substrate,
531 along with the operating conditions of the AD process (e.g. pH and temperature).
532 Focusing on direct factors, a better understanding of the interactions between BC and
533 FAN/TAN is a key step to identify its physico-chemical properties able to maximise the
534 ammonia removal. The mechanisms for ammonia adsorption on BC from wastewater and
535 digestate have been studied in literature (Table 5), resulting in promising values of
536 ammonium adsorption capacity (up to hundreds of mg NH_4-N g^{-1} BC). Yin et al. (2017)
537 [112] reported that physical sorption could be supported by high SSA and large porous
538 structure. However, various studies suggested that porosity and SSA may not be the
539 predominant factors in ammonium adsorption [154,155]. For instance, ion exchange may
540 occur between acidic functional groups on BC surface and ammonium [112,156,157],
541 and CEC could have a major role in enhancing the ammonium adsorption capacity of BC
542 [157]. Zhang et al. (2014) [158] found that BC derived from pyrolysis of corn cob at 400
543 °C exhibited higher ammonium adsorption capacity than those produced at 600 °C due to
544 the presence of functional groups with higher acidity. Thus, the definition of the proper
545 pyrolysis temperature and the other control parameters is crucial for enhancing the
546 adsorption capacity of BC.
547 In conclusion, various studies reported the potential of BC in alleviating ammonia
548 inhibition (Tables 4 and 5) through different mechanisms. The direct adsorption of
549 ammonia on BC may contribute to the mitigation of ammonia inhibition. However,
550 further studies are required to clarify the effective role of direct mechanisms in complex
551 AD systems in presence of other phenomena, i.e. the close bond between ammonia and

552 VFAs inhibition. In some cases the direct removal of ammonium may not be the main
553 contribution to the mitigation of ammonia inhibition by BC [44,82,153]. Instead, other
554 indirect mechanisms (immobilization and faster acclimation of biomass, DIET) have been
555 suggested in literature and will be discussed in the next sections.
556

557 Table 4. A summary of selected works focusing on ammonia/ammonium inhibition mitigation by BC in AD processes (FAN: free ammonia
558 nitrogen; TAN: total ammonia nitrogen).

Biochar					Anaerobic digestion							Reference
Feedstock	Process: temperature [°C]	Dose of biochar	Substrate	Inoculum	Inoculum to substrate ratio (VS basis)	Temperature [°C]	pH	Critical TAN conc. or as specified [mg L^{-1}]	Critical FAN conc. or as specified [mg L^{-1}]	Ammonia removal by biochar	Results and comments	
Fruitwood	Pyrolysis: 800-900°C	10 g L^{-1}	Glucose solution (6 g L^{-1})	Granular sludge from AD of paper mill wastewater	1:6	35	7	260 3500 7000	- - -		• ↑ Specified CH_4 prod. rates increased by 18.6%, 10.1% and 23.5% respectively • ↓ Lag phase by 30.4%, 12.7% and 23.8% respectively	[44]
1:2 (v/v) mix: - paper sludge - wheat husks	Pyrolysis: 500°C	6.67% w/w (2 g BC per 30 g inoculum)	-	Meso. AD (TS = 4.05%) + Ammonium carbonate	Only 30 g of inoculum	42	7.66 7.73 7.93 7.84 8.07	1626 2126 3126 4126 6626	- - - - -	2.4 mg TAN g^{-1} BC 2.0 mg TAN g^{-1} BC 4.2 mg TAN g^{-1} BC 4.5 mg TAN g^{-1} BC 6.8 mg TAN g^{-1} BC	• No clear effect on biogas production was observed	[41]
Macadamia nut shells	Pyrolysis: 350°C	33.3 g L^{-1}	Food waste (+ water + $NaHCO_3$)	AD from UASB (SS =34 g	-	Room temperature		1500	-		• ↑ COD removal from 78% without BC to 90% with BC	[43]
Corn stover	Gasification	1.82, 2.55, 3.06, 3.64 g BC g^{-1} TS sludge	WWTP sludge	Thermo WWTP AD	2:1	55	7.5	1100 (total N)	600 (NH_3-N)		• CH_4 yield, biomethanation rate constant and ↑ max CH_4 prod. rate up to 7.0%, 8.1% and 27.6% respectively • ↑ NH_3-N concentration by 41.5% after AD without BC, while by 0.2-18.1% with BC	[151]
Pine pellets	Gasification	2.49, 4.97 g BC g^{-1} TS sludge	WWTP primary sludge	Meso. and thermo. WWTP AD	2:1	37, 55	7.2-7.3	750 (total N)	400-450 (NH_3-N)		• ↑ CH_4 yield by 3.9-9.5% • ↑ NH_3-N concentration by 67.0% after AD without BC, while by -7.2 to 4.7% with BC	[33]

White oak pellets		2.20, 4.40 g BC g^{-1} TS sludge	TS = 1.25% (inoc +subs)	TS = 1.25% (inoc +subs)							• ↑ CH_4 yield by 5.7-9.6% • ↑ NH_3-N concentration by 67.0% after AD without BC, while by -7.2 to 4.7% with BC	
Corn stover	Gasification: 850°C	0.25, 0.375, 0.5, 1.0 g d^{-1}	Primary sludge + WAS (TS = 7.01%)	WWTP AD from TPAD: 1 stage (TS = 6.14%) 2 stage (TS = 3.77%)	2:1	55	7.4 (stage 1); 5.3-6.0 (stage II)	-	-	6.2-13.2%	• ↑ CH_4 content by 13.7-25.3% • ↑ CH_4 prod. rate by 5.5-36.9%	[34]
Pine								-	-	3.6-11.2%	• ↑ CH_4 content by 0.7-9.1% • ↑ CH_4 prod. rate by -2.3-16.6%	
Wheat bran pellets	Pyrolysis: 800°C	25 g L^{-1}	Food waste fermentate	Anaerobic methanogenic culture (from WAS AD)	-	20	7.5		200–250 (NH_3-N)		• After acclimation: ↑ rate of VFAs degradation and ↓ lag-phase; • No adsorption of ammonia by BC	[45]
Coppiced woodlands	Pyrolysis: 500°C											
Orchard pruning	Pyrolysis: 500°C											
Wheat straw	Pyrolysis: 350, 450, 550°C	5% w/w (chicken manure)	Chicken manure (+ water)	Chicken manure meso. AD	Inoculum: 20% of WV of AD reactor	35	Initial: 6.7-7.6	3450-3540 (average)	472-600 (max)		• ↑ Cum. CH_4 yield • ↓ TAN compared to control	[82]
Fruit wood	Pyrolysis: 350, 450, 550°C						Initial: 6.7-7.0	3440-3650 (average)	421-634 (max)	up to 25% TAN	• ↑ Cum. CH_4 yield up to 69% • ↓ TAN compared to control • ↓ FAN up to 58% compared to control	
Air-dried chicken manure	Pyrolysis: 350, 450, 550°C						Initial: 6.9-7.3	3880-3960 (average)	496-701 (max)		• ↑ Cum. CH_4 yield • ↓ TAN compared to control	

559

560

561 Table 5. Ammonium adsorption capacity of different BCs (NA: not available)

Biochar production		Biochar properties				Adsorption			Reference
Feedstock	Pyrolysis temperature [°C]	BET-SA [$m^2 g^{-1}$]	pH	CEC [$cmol_c\ kg^{-1}$]	Total pore volume [$mL\ g^{-1}$]	Source of NH_4^+-N	Initial NH_4^+-N [$mg\ L^{-1}$]	NH_4^+ adsorption capacity [mg NH_4^+-N g^{-1} biochar]	
Oak wood	400-450	NA	9.9	59.4 ± 8.1	NA	Ammonium solution	1000	100.9 ± 3.4	
Oak wood	-	NA	9.7	105.8 ± 12.1	NA		-	129.4 ± 34.8	
Greenhouse waste	-	NA	10.6	109.5 ± 21.8	NA	-	-	118.2 ± 26.9	
Municipal waste	-	NA	9.5	65.7 ± 16.2	NA	-	-	137.3 ± 0.6	
Presscake from AD	-	NA	10.3	51.0 ± 5.5	NA	-	-	105.8 ± 11.5	[154]
Oak wood	600-650	NA	10.3	76.6 ± 0.7	NA	-	-	114.4 ± 3.4	
Oak wood	-	NA	8.6	65.2 ± 20.2	NA	-	-	123.5 ± 28.7	
Greenhouse waste	-	NA	11.0	146.2 ± 32.3	NA	-	-	99.3 ± 28.5	
Municipal waste	-	NA	10.2	67.9 ± 12.5	NA	-	-	128.3 ± 6.7	
Presscake from AD	-	NA	10.1	52.6 ± 11.5	NA	-	-	136.2 ± 18.1	
Hardwood	600	147.0	9.80	NA	0.176	AD slurry	500–580	114.2	
Corncobs	-	23.0	8.92	NA	0.098	-	-	108.9	[159]
Mixed sawdust	-	6.80	8.60	NA	0.038	-	-	24.7	

Mixed wood	600	273.623	9.80	NA	0.176	Swine manure AD slurry	1400 mg N L^{-1}	44.64 ± 0.602	
Rice husk	/	10.995	7.80	NA	0.038	-	-	39.8 ± 0.54	[155]
1:2 (v/v) mix: - paper sludge - wheat husks	500	NA	NA	NA	NA	During anaerobic digestion	1626 mg TAN kg^{-1}	2.4 mg TAN g^{-1}	
		-	-	-	-	-	2126 mg TAN kg^{-1}	2.0 mg TAN g^{-1}	
		-	-	-	-	-	3126 mg TAN kg^{-1}	4.2 mg TAN g^{-1}	[41]
		-	-	-	-	-	4126 mg TAN kg^{-1}	4.5 mg TAN g^{-1}	
		-	-	-	-	-	6626 mg TAN kg^{-1}	6.8 mg TAN g^{-1}	
Fruitwood	800-900	NA	NA	NA	NA	NH_4Cl solution	NA	2-3 mg N g^{-1}	[44]

562

563 *4.3. Effects on microbial populations*

564 Many authors reported the positive effects of BC on microbial populations in AD (Table
565 6). In semi-continuous and continuous AD experiments, BC addition improved methane
566 production [34] keeping it stable even with rising OLRs [29,49] and resulted in higher
567 COD removal rates [43,50,51].

568 Although there is a good agreement among the studies in terms of enhancement of AD
569 process performances (11-30 % reduction of lag phases and 11-50 % increments of
570 methane production rates) (Table 6), there is not a common hypothesis to explain BC
571 influence on microbial populations, and different possible mechanisms are proposed as
572 follows.

573 *4.3.1. Microbial attachment and acclimation*

574 Immobilization and acclimation of balanced microbial consortia on various support media
575 are commonly adopted for counteracting various drawbacks of AD processes [160],
576 thanks to the intensification of syntrophic conversion relationships, along with a major
577 resistance to inhibition effects [161]. Wang et al. (2018) [50] found that BC acted as an
578 inert core for microbial aggregation, resulting in a higher microbial growth rate and
579 accelerating sludge granulation. Cooney et al. 2016 [53] investigated the possibility of
580 accelerating biofilm formation by adding BC during the start-up of a packed bed
581 anaerobic digester at pilot scale. In a relatively short time, the AD system reached stable
582 and good performances, suggesting the rapid development of biofilms rich in active
583 methanogens.

584 High SSA, proper porosity structure and particle size, superficial hydrophobicity seemed
585 to be important properties favouring microbial immobilization [12,52]. Further,
586 conductive materials may act as ideal support media due to their surface hydrophobicity

and porous structure [54,55]. In particular, macropores can help the attachments of bacterial cells [19,162,163]. Lü et al. (2016) [44] explored the influence of different particle sizes of BC (2-5 mm, 0.5-1 mm, 75-150 μm) on the microbial distribution during the AD of glucose under ammonium stress. They stated that bacteria could access more easily fine particles than coarse particles. As a consequence, the attachment and colonization of microbial populations on BC can limit the risks of wash-out, accelerate the acclimation of microbes during substrate-induced inhibition, reduce the distance between syntrophic bacteria and methanogens, facilitate interspecies electron transfer and exchanges of VFAs or other metabolites [16,36,137]. Li et al. (2018) [46] found that methanogens survived under acidic stress in presence of BC during co-digestion of FW and WAS. Further, the immobilization of microbes could significantly attenuate ammonia inhibition [43,44]. The colonization of porous materials by microbes can alter the dominant species, making them more resistant and more rapidly acclimatized to substrate-induced inhibition [29,36,164]. Magnetic BC favoured the enrichment of acido/acetogens and methanogens absorbed on its surface shortening the microbial contact distance, thus VFAs produced by acido/acetogen bacteria could be more quickly transported to methanogens than in control digesters during AD of OFMSW in batch tests [16,139]. The distance of less than 1 μm has been reported to be essential for the oxidation of VFAs and hydrogen production [19,165].

4.3.2. Selective colonization of functional microbes

The effect of BC addition on microbial communities was investigated with the aim of identifying the most abundant bacterial and archaeal populations and, indirectly, the main interspecies interactions (Table 6). In detail, most studies focused on: biofilm formation [26,48,53]; shifts of microbial populations [28,34,46,47]; selective enrichment of

611 microbial -DIET partners [38,44,49,50]; promotion of DIET [38,44–46,49,51,139]. The
612 relevant anaerobic bacteria and archaea enriched in BC amended digesters are reported
613 in Table 7, together with BC properties, substrate and inoculum used in AD tests. Many
614 bacterial species were found in reactors supplemented with BCs, none of them identified
615 as more recurrent. Among archaeae, most studies identified *methanosaeta*,
616 *methanosarcina*, *methanobacterium*, and *methanolinea* species in BC amended reactors.
617 Different studies [44,48,51] investigated the spatial distribution of bacteria and archaea
618 by dividing sludge samples into different fractions, from suspended to attached to BC. Lü
619 et al. (2016) [44] postulated an explanation for the spatial distribution of methanogens
620 into BC pores by their cell morphology and dimension. The short fibrous form of
621 Methanosaeta (0.8-7 μm in size) could explain its attachment into internal and external
622 pores, while the long fibrous form of Methanobacterium (1.2-120 μm in length) could
623 limit its penetration into BC pores [44,166].

624 *4.3.3. Promotion of syntrophic metabolisms*

625 Many studies (Table 7) suggested that BC addition may improve electron transfer
626 mechanisms between anaerobic bacteria and archaea closely attached to BC surface. The
627 overall AD efficiency depends on effective syntrophic interactions between bacteria and
628 methanogens exchanging electrons to satisfy their energy requirements [56], happening
629 through various routes:

630 - Indirect interspecies electron transfer (IIET) via soluble (i.e. hydrogen, formate,
631 acetate) [167,168] and insoluble (humic substances) [169,170] compounds;
632 - Direct interspecies electron transfer (DIET) via electrical conductive pili, membrane-
633 bound electron transport proteins, and conductive materials (i.e. magnetite, biochar,
634 granular activated carbon, carbon cloth) [171–173].

635 In IIET hydrogen and formate operate as electron shuttles between syntrophic-producing
636 bacteria and consuming-methanogens [56]. Diffusion regulates the transfer of a
637 metabolite between microorganisms, as defined by Fick's Law [174]: the shorter the
638 distance, the higher the flux of metabolites between microbes. Thereby, when cells
639 aggregate the rate of interspecies hydrogen transfer is enhanced by the moment anaerobic
640 bacteria and methanogenic archaea form compact structures acting as an organ [174,175].
641 However, the diffusion of soluble metabolites is considered a relatively slow mechanism
642 of energy and information transfer [173] and hydrogen IET is regarded as a bottleneck in
643 methane production [171]. On the contrary, DIET consists in the formation of an electric
644 current between electron-donating and electron-acceptor microorganisms without the
645 mediation of electron shuttles [56]. DIET could be faster and more specific compared to
646 IIET [173,176]. Park et al. (2018) [171] reported that direct exchange of electrons via
647 conductive pili was observed in co-cultures between *geobacter metalliriducens* and
648 *geobacter sulfurreducens* [176], *methanosaeta harundinacea* [177], or *methanosarcina*
649 *barkeri* [178]. Conductive materials such as magnetite [179], GAC [180], and BC [57]
650 were shown to effectively mediate DIET between syntrophic partners.
651 Based on changes in the microbial community composition, many studies justified the
652 enhancement of AD activity by means of the improvement of hydrogen and formate
653 interspecies transfer mechanisms or, more frequently, by DIET via conductive biochar
654 (Table 7). These findings are usually based on indirect observations, i.e. the enrichment
655 of bacterial and archaeal species able to participate to DIET function as potential partners.
656 Martinez et al. (2018) [47] found an enrichment of homoacetogenic bacteria, as
657 *Clostridium, Eubacterium* and *Syntrophomonas*, and H_2 using methanogens through the
658 analysis of microbial communities in digesting WAS and orange peels with BC,

659 suggesting the formation of co-cultures enhancing methane production. Zhao et al. (2016)
660 [51] observed the selective enrichment on BC of *Geobacter* and *Methanosaeta* during
661 AD of synthetic wastewater with butyrate and propionate in UASB reactors. They
662 suggested that butyrate and propionate could be degraded via DIET in the presence of a
663 conductive material, and they found abundance of *Syntrophomonas* and *Smithella*,
664 concluding that the metabolism via interspecies H_2 transfer for butyrate and propionate
665 degradation was probably present. Wang et al. (2018) [50] showed that the microbial
666 community analysis in a BC amended reactor during AD of synthetic wastewater resulted
667 in the selective enrichment of potential DIET-partners, as *Geobacter* and *Bacteroidetes,*
668 as well as archaea *Methanosaeta* and *Methanosarcina*. They suggested that BC could
669 enhance DIET among electrogenic microbes and archaea, improving the electron transfer
670 characteristics of granular sludge, as well as COD removal and methane yield. Wang et
671 al. (2018) [38] found that the addition of different BC doses increased methane production
672 rate and shortened the lag phase during mesophilic AD of dewatered WAS and FW.
673 According to the authors, BC counteracted the pH decrease due to VFAs accumulation
674 through its buffering capacity, and it seemed to promote DIET.
675 Aside from physical properties as SSA and porosity, favouring microbial colonization,
676 other chemical and conductive characteristics of BC may be crucial in the promotion of
677 electrons transfer. The role of electrical conductivity (EC) of BC in AD has been
678 investigated in literature[59]. EC of digestate has been reported to increase in presence of
679 BC [50,151]. However, the EC of digestate seemed unrelated to the conductivity of BC,
680 which varies depending on the metabolism and composition of microbial species [56].
681 The capability of BC in promoting DIET appeared to be comparable to that of GAC, even
682 if the EC of BC was roughly 1000 times lower [57,171]. Barua and Dhar (2017) [181]

683 reported that multi-species aggregates from anaerobic digesters exhibited conductivity
684 ranging 0.2-36.7 μS cm^{-1}, suggesting its relation with DIET via conductive pili . Martins
685 et al. (2018) [56] stated that conductive materials could have a similar role of humic
686 substances in DIET, acting as electron shuttles by receiving and donating electrons. Wang
687 et al. (2019) [49] suggested that BC from sawdust may act as a temporary electron
688 acceptor for VFAs oxidation during thermophilic AD. They found a significantly higher
689 and more stable methane yield at higher OLR values during anaerobic co-digestion in
690 semi-continuous mode with the addition of BC from sawdust, while they did not show
691 any enhancement of AD with the addition of BC from sewage sludge. The main effects
692 of sawdust BC seemed to be the enhancements of microbial activities and syntrophic
693 oxidation of VFAs. The EC of both BCs was similar, suggesting it was not a determinant
694 factor in the promotion of syntrophic oxidation of VFAs. Instead, the authors speculated
695 that the presence of redox-active phenazine structures in the BC from sawdust could
696 promote VFAs degradation via DIET. Thereby, for better investigating whether BC from
697 sawdust could substitute hydrogen as electron acceptor in syntrophic oxidation of VFAs,
698 they conducted a series of batch experiments with butyrate or propionate as substrates in
699 which methanogenesis was inhibited. The control reactors did not show degradation of
700 butyrate and propionate, while the addition of BC stimulated their oxidation as well as
701 the production of acetate, supporting the hypothesis of the electron-accepting capacity of
702 BC in the syntrophic process.
703 The adoption of a further control in AD tests amended with a non-conductive material
704 can be crucial to investigate whether the stimulatory effects of BC on methane production
705 can be more closely linked to its physical properties (i.e. SSA and porosity) rather than
706 its electrical properties [56]. This was evident in the study of Cruz Viggi et al. (2017)

707 [45], where they introduced two controls without BC and with non-conductive silica sand
708 for AD of FW. They found that VFAs degradation and methane production were faster
709 in the case of BC amended reactors than both the control reactors, suggesting the
710 predominant influence of the electrical properties of BCs.

711 Table 6. A summary of selected works focusing on positive effects of BC on microbial populations in AD processes

Biochar		Anaerobic digestion							References
Feedstock	Production	Dose of biochar	Substrate	Inoculum	Temperature [°C]	Experimental mode	Results	Possible mechanisms	
Sawdust	Pyrolysis: • 500°C • 1 h • 20°C min^{-1}	10 g L^{-1}	Food waste (TS = 94.2 g L^{-1})	WAS (TS = 89.1 g L^{-1})	55°C	Batch V = 120 mL S/I (VS) = 0.25 - 3	By ↑ OLR: • ↓ lag time • ↑ CH_4 prod. rate	• ↑ buffer capacity • Microbial attachment and acclimation on BC • Promotion of DIET • Selective succession of microbes	[46]
Pine sawdust	Pyrolysis: • 650°C • 20 min	8.3 - 33.3 g L^{-1}	Food waste (bread) (TS = 61.2%)	WWTP-sludge (heated at 95°C)	35°C	Batch V = 100 mL TPAD	1st phase: • ↓ lag phase • Faster VFAs generation • ↑ H_2 prod. rate • ↑ Cum. H_2 prod. 2nd phase: • ↓ lag phase (41-45%) • Faster VFA degradation • ↑ CH_4 prod. rate	1st phase: • Promotion biofilm formation • Providing temporary nutrients • Buffering pH by BC 2nd phase: • Promotion methanogenic biofilm formation • No buffering pH by BC	[26]
Macadamia nut shells	Pyrolysis: • 350°C • 2 h	33.3 g L^{-1}	Food waste + water + (↑ $N\text{-}NH_4$ conc.)	AD from	Room temperature	CIC reactor V = 4.6 L HRT=16 h	• ↑ COD removal by 15%	• ↓ NH_3 inhibition by BC • ↑ Alkalinity by BC • ↓ VFAs accumulation	[43]

Biochar		Anaerobic digestion							References
Feedstock	Production	Dose of biochar	Substrate	Inoculum	Temperature [°C]	Experimental mode	Results	Possible mechanisms	
	• 10°C min^{-1}			(SS = 34 g L^{-1})				• ↑ Selective enrichment of functional microbes • Microbial attachment and acclimation on BC	
Sawdust	Pyrolysis: • 500°C • 1.5 h • 10°C min^{-1}	2 - 15 g L^{-1}	Dewatered WAS + Food waste (TS = 8.8%) + water	Meso. AD from brewery factory (TS = 6.8%)	35°C	Batch Serum bottles WV = 90 mL S/I = 0.75 - 3 (VS)	• ↓ lag phase by 27.5–64.4% • ↑ Max CH_4 prod. rate by 22.4%–40.3%	• Buffer capacity by BC (alleviate ↓ pH due to ↑ VFAs) • ↑ DIET by BC (temporary electron acceptor, due to the richness of surface functional groups) • Selective enrichment of microbial DIET-partners by BC	[38]
Sawdust	Pyrolysis: • 500°C	15 g L^{-1}	Food waste + Sewage sludge (TS = 9.2%) FW/Sludge = 4:1 (TS)	Brewery Meso. AD (TS = 5.2%)	55°C	Semi-continuous Serum bottles WV = 150 mL ↓ HRT, ↑ OLR	• ↑ CH_4 yield by 16.0%−55.2% • Stable CH_4 prod. at ↑ OLRs	• ↑ VFAs syntrophic oxidation by BC • High SA of BC → microbial attachment (?), closer association of syntrophic partners • Electroactive functional groups of BC → stimulation of DIET (?)	[49]
Corn stover	Gasification: • 850°C	0.25 - 1.0 g d^{-1} (2^{nd} phase)	Primary sludge + WAS (TS = 7.01%)	WWTP AD	55°C	Semi-continuous V = 500 mL TPAD:	• ↑ % CH_4 by 13.7-25.3% • ↑ CH_4 prod. rate by 5.5-36.9%	• Adsorption and precipitation of CO_2 by BC • ↓ TAN • ↑ Alkalinity • ↑ Macro-/micro-nutrients in digestate • Shift in bacterial community	[34,182]

Biochar		Anaerobic digestion							References
Feedstock	Production	Dose of biochar	Substrate	Inoculum	Temperature [°C]	Experimental mode	Results	Possible mechanisms	
				TPAD: 1 ph. (TS = 6.14%) 2 ph. (TS = 3.77%)		1) HRT = 5, 15 d 2) HRT = 13 - 30 d		• Inhibition at high BC doses	
Pine	-	-	-	-	-	-	• ↑ % CH_4 by 0.7-9.1% • ↑ CH_4 prod. rate by 2.3-16.6%		
Corn stover	Gasification	1.82 -3.64 g BC g^{-1} TS sludge	WWTP sludge	Thermo. WWTP AD	55°C	Batch V = 600 mL 26 days	• ↑ % CH_4 (88.5-96.7%) • ↑ CH_4 yield	• ↑ buffer capacity • ↑ electrical conductivity in digester (+37%) → ? ↑ extracellular electron transfer • ↓ NH_3 inhibition • CO_2 sequestration by BC • ↑ macro-/micro-nutrients in digestate	[151]
Rice husks	Gasification: • 900-1000°C	1%, 3% w/w	Cattle manure + water (TS = 5%)	-	35°C	Batch V = 1400 mL	• ↑ Biogas prod. by 31% by 1% BC • ↓ % CH_4 by 7% by 1% BC • No benefits by 3% BC	• ? Microbial biofilm formation on BC	[30]

Biochar		Anaerobic digestion							References
Feedstock	Production	Dose of biochar	Substrate	Inoculum	Temperature [°C]	Experimental mode	Results	Possible mechanisms	
Rice husks	Gasification: • 900-1000°C	1%, 3% w/w	Cattle manure + water (Mix: TS = 5%)	-	25-30°C	Semi-continuous WV = 12 L HRT = 20 days	• ↑ Biogas prod. by 4-5% by BC • ↓ % CH_4	• ? Not enough time for biofilm formation	[31]
Dry dairy manure	Pyrolysis: • 350°C • 3 h • 10°C min^{-1}	0, 1, 10 g L^{-1}	Dry dairy manure	Inoculum from lagoon, fed with dried manure (TS = 115.85 g L^{-1})	20°C	Batch: Serum bottles V = 280 mL S/I = 1 (VS)	• ↑ CH_4 yield up to 26.5% • ↓ lag phase • ↓ total VFAs	• No biofilm formation on BC (?) • No effects on DIET by BC (?) • ↑ Alkalinity and ↑ pH (buffer capacity)	[27]
-	-	-	-	-	35°C	-	• ↑ CH_4 yield up to 24.9% • ↓ lag phase • ↓ total VFAs	• ↑ Alkalinity and ↑ pH (buffer capacity)	
-	-	-	-	-	55°C	-	• ↑ CH_4 yield up to 24.7% • ↓ lag phase • ↓ total VFAs	• ↑ Alkalinity and ↑ pH (buffer capacity)	
Vineyard prunings	Pyrolysis: • 550°C	10, 30 g L^{-1}	Co-digestion:	WWTP AD	37°C	Batch: • V = 250 mL	Batch: • ↓ lag phase	• Promotion of synthrophic metabolism by BC • Adsorption of inhibitors	[47,183]

Biochar		Anaerobic digestion							References
Feedstock	Production	Dose of biochar	Substrate	Inoculum	Temperature [°C]	Experimental mode	Results	Possible mechanisms	
			• Orange peels (TS = 311g kg^{-1}) • Sewage sludge (TS = 28.7g kg^{-1})	(TS = 35.5 g kg^{-1})		Semi-continuous • V = 3 L • HRT = 10-30 days	• ↑ CH_4 prod. Semi-continuous: • ↑ CH_4 prod.	• Adhesion and growth of microorganisms by BC SA	
Coconut shell	Pyrolysis: • 450°C	1:1 (TS)	Citrus peel (TS = 16.6%)	WWTP AD (TS = 11.0 %)	35°C	Batch V=500 mL S/I = 0.31 - 0.33 (VS)	• ↓ lag phase • ↑ Cum. CH_4 prod.	• Limonene adsorption by BC	[40]
Rice husk	-	1:1 (TS)	-	-	-	-	• ↓ lag phase • ↑ Cum. CH_4 prod.	• Limonene adsorption by BC • Adhesion and growth of microbes on BC	
Wood	-	1:1; 1:2; 1:3; 2:1 (TS)	-	-	-	-	• ↓ lag phase • ↑ Cum. CH_4 prod.	• Limonene adsorption by BC • Adhesion and growth of microbes on BC	

Biochar		Anaerobic digestion							References
Feedstock	Production	Dose of biochar	Substrate	Inoculum	Temperature [°C]	Experimental mode	Results	Possible mechanisms	
Rice straw + $FeCl_3$ (3.2 g $FeCl_3$:100 g rice-straw)	In $FeCl_3$ solution: • 2h Carbonization: • 500°C • 2h	0.5% w/w	OFMSW + water (TS = 1.64%)	OFMSW thermo. AD + water (TS = 2.19%)	35°C	Batch Serum bottles V = 500 mL, S/I = 1 (VS)	• ↓ lag phase • ↑ CH_4 prod. by 11.69%	• No effects on NH_3 by BC • No effects on pH by BC • ↑ syntrophic associations of bacteria on BC • (?) DIET by high conductivity of BC	[139]
Rice straw	Carbonization: • 500°C • 2h	-	-	-	-	-	• ↓ lag phase • ↓ CH_4 prod.	• No effects on NH_3 by BC • No effects on pH by BC	
Cow manure	Pyrolysis: • 500°C • 4 h • 100°C h^{-1}	2 – 14 g L^{-1}	Dry beer lees (TS = 62.5%)	Meso. WWTP AD (TS = 36.7%)	35°C	Batch WV = 150 mL TS = 25% S/I = 3 (TS)	• ↓ lag phase • ↑ Max cum. CH_4 prod. up to 82.9%	• Promotion of DIET by BC conductive properties (?) • Microbial colonisation and biofilm formation on BC (?) • ↑ Alkalinity and ↑ pH (buffer capacity) • Selective enrichment of methanogens by BC	[28]
-	-	-	-	Thermo. WWTP AD (TS = 38.5%)	55°C	-	• ↓ lag phase • ↑ Max cum. CH_4 prod. up to 47.2%	-	
Rice straw	Pyrolysis: • 500°C	4 g L^{-1}	Synthetic wastewater	WWTP sludge	35°C	UASB	UASB: • ↑ COD removal rate	• No effects on pH by BC • BC inert core for microbial aggregation	[50]

Biochar		Anaerobic digestion							References
Feedstock	Production	Dose of biochar	Substrate	Inoculum	Temperature [°C]	Experimental mode	Results	Possible mechanisms	
				(SS = 25.2 g L^{-}		• Continuous mode • V = 5500 mL • HRT = 12 h, 12-6 h Batch • Serum bottles • V = 550 mL	• ↑ VFAs degradation • ↑ gran. sludge conductivity and quality Batch: • ↓ lag phase by 28.6% • ↑ biogas yield • ↑ $\%CH_4$	• Selective enrichment of microbial DIET-partners by BC	
-	Biochar	-	Grease trap waste wastewater (TSS = 1.04 g L^{-1})	-	37°C	Biochar packed bed anaerobic digester • V: 900 L +1500 L+ 1500 L • ↓ HRT (3.1 – 1.8 days)	• COD removal:68% • Total VFAs: from 4.7 (feed) to 1.46 g L^{-1} (effluent) • $\%CH_4$ > 60% • Start-up: 59 days	• ↑ Methanogenic biofilm communities on BC • BS as packing material for growth and retention of biofilm	[53]

Biochar		Anaerobic digestion							References
Feedstock	Production	Dose of biochar	Substrate	Inoculum	Temperature [°C]	Experimental mode	Results	Possible mechanisms	
Wheat bran pellets	Pyrolysis: • 800°C • 3h	25 g L^{-1}	Food waste fermentate	Methanogenic culture (from WAS digestate)	20°C	Batch V = 120 mL	After acclimation: • ↑ rate of VFAs degradation • ↓ lag-phase	• No effects on pH via BC • No effects on NH_3 via BC • Promotion of IET by BC	[45]
Coppiced woodlands	Pyrolysis: • 500°C	-	-	-	-	-		-	
Orchard pruning	Pyrolysis: • 500°C	-	-	-	-	-		-	
Fruitwood	Pyrolysis: • 800-900°C	10 g L^{-1}	Glucose (6 g L^{-1})	AD gran.	35°C	Batch Serum bottles	• ↓ lag phase by 5.9-23.9% • ↑max CH_4 prod. rate by 23.5-47.1% • Faster VFAs degradation	• NOT NH_4 adsorption • NOT ↑ buffer capacity • DIET promotion via BC • Affinity of methanogens with BC	[44]

Biochar		Anaerobic digestion							References
Feedstock	Production	Dose of biochar	Substrate	Inoculum	Temperature [°C]	Experimental mode	Results	Possible mechanisms	
				Ammonium: 0.26, 3.5, 7 g-N L^{-1}					
Fruit wood	Pyrolysis: • 800°C	10 g L^{-1}	Nutrient solution + glucose (2 - 8 g L^{-1})	Meso. pulp sewage digestate (1 g VS L^{-1})	35°C	Batch Serum bottles V = 500 mL	• ↓ lag phase by 11.4-30.3% • ↑ Max CH_4 prod. rate by 5.2-86.6% • ↑ VFAs production and degradation	• Selective colonization of functional microbes by BC • Not ↑ buffer capacity • ? Biofilm growth on BC • ? Promotion of DIET or Hydrogen IET by BC	[48]
Pine wood	Pyrolysis: • 600°C • 2h	5 g L^{-1}	Synthetic wastewater with butyrate	WAS digestate (TSS = 13.1 g	37°C	UASB WV = 1000 mL	• ↑ CH_4 prod. rate by 25% • ↑ COD removal	• ↑ Butyrate degradation via DIET in UASB via BC • Selective enrichment of microbial DIET-partners by BC	[51,57]
			Synthetic wastewater with propionate				• ↑ CH_4 prod. rate by 16% • ↑ COD removal	• ↑ Propionate degradation via DIET in UASB via BC • Selective enrichment of microbial DIET-partners by BC	

Biochar		Anaerobic digestion							References
Feedstock	Production	Dose of biochar	Substrate	Inoculum	Temperature [°C]	Experimental mode	Results	Possible mechanisms	
-	Biochar	2.5 g L^{-1}	Synthetic wastewater with ethanol	WAS digestate (TSS = 13.1 g	37°C	UASB WV = 1000 mL ↓ HRT (24 - 8 h)	• ↑ COD removal: ≥ 93% (control: 75-83%) • ↑ CH_4 prod. rate	• (?) Promotion syntrophic metabolism via DIET with BC in UASB reactors	[29]

CIC: controlling internal circulation; COD: chemical oxygen demand; DIET: direct interspecies electron transfer; FW: food waste; HRT: hydraulic retention time; IET: interspecies electron transfer; OLR: organic loading rate; OFMSW: organic fraction of municipal solid waste; SA: surface area; S/I: substrate to inoculum ratio; SMP: specific methane potential; SS: suspended solids; TPAD: two phased anaerobic digestion; TSS: total suspended solids; UASB: up-flow anaerobic sludge blanket; VFA: volatile fatty acid; WAS: waste activated sludge; WWTP: wastewater treatment plant; WV: working volume; V: volume.

712

713

714 Table 7. A summary of studies reporting the selective enrichment of bacteria and archaea by BC addition during AD processes

Biochar production		Biochar properties			Anaerobic digestion					Reference
Feedstock	Pyrolysis temperature [°C]	BET-SSA [m^2g^{-1}]	Electrical conductivity [S m^{-1}]	Total pore volume [cm^3 g^{-1}]	Temperature [°C]	Substrate	Identification technique	Enriched Bacteria	Enriched Archaea	
Wheat bran pellets	800	55 ± 1	49.9	0.0445	20	Food waste fermentate	FISH- CLSM		More Methanosarcina-like Archaea rather than Methanosaeta like Archaea	[45]
Coppiced woodlands	500	61 ± 1	1.6	0.0483						
Orchard pruning	500	13.7 ± 0.5	0.5	0.0165						
Macadamia nut shells	350	12.7	-	-	Room temperature	Food waste + water	16S rRNA sequencing	Bacteroidales Anaerolineales Syntrophobacterales	Methanoregulaceae Methanotrichaceae Methanobacteriaceae	[43]
Fruitwoods	800-900	-	-	-	35	Glucose	16S rRNA sequencing	Enterobacteriaceae	Methanobacterium Methanosaeta Methanosarcina	[44]
Fruit wood	800	-	-	-	35	Glucose	16S rRNA sequencing	Syntrophomonas Clostridium Clostridiaceae	Methanobacterium Methanosaeta Methanosarcina	[48]
Rice straw + $FeCl_3$ (3.2 g $FeCl_3$:100 g rice-straw)	500	51.14	-	0.0328	35	OFMSW + water	16S rRNA sequencing	Bacteroides Clostridiaceae Porphyromonadaceae Moraxellaceae	Methanosarcina Methanobacterium OTU in Methanomicrobiales Methanosaeta	[139]
Rice straw	500	111.5	-	-	35	Synthetic wastewater	16S rRNA sequencing	Bacteroidetes unclassified (23.65%) Bacteroidales unclassified (9.19%)	Methanosaeta (77.18%) Methanosarcina (11.65%)	[50]

								Treponema (6.43%) Smithella (5.56%) Brooklawnia (5.45%) Geobacter (5.42%)		
Sawdust	500	248.6	-	-	35	Dewatered WAS + food waste + water	16S rRNA sequencing	Anaerolineaceae Porphyromonadaceae	Methanosaeta Methanobacterium Methanolinea	[38]
Cow manure	500	112.6	-	0.0156	35	Dry beer lees	16S rRNA sequencing	Chloroflexi Bacteroides Proteobacteria	Methanospirillum Methanosarcina Methanolinea	[28]
Vineyard prunings	550	240 ± 4.8	-	-	37	Orange peels	16S rRNA sequencing	Bellilinea Trepomena Clostridium Petrimonas Proteiniphilum Bacteroides	Methanosaeta Thermogymnomonas Methanolinea Methanofollis	[47]
Vineyard prunings	550	240 ± 4.8		-	37	Sewage sludge	16S rRNA sequencing	Clostridium Longilinea Curvibacter Eubacterium Syntrophomonas	Methanosaeta Methanolinea Thermogymnomonas Methanobacterium	
Pinewood	600	209	.33 µS cm^{-1}	-	37	Synthetic wastewater with butyrate	16S rRNA sequencing	Attached sludge: Geobacter Thermanaerovibrio Syntrophomonas	Attached sludge: Methanosaeta Methanosarcina Methanospirillum	[51]
Pinewood	600	209	4.33 µS cm^{-1}	-	37	Synthetic wastewater with propionate	16S rRNA sequencing	Attached sludge: Geobacter Smithella	Attached sludge: Methanosaeta Methanobacterium	

								Syntrophus	Methanosphaerula	
Biochar	-	-	-	-	37	Grease trap waste wastewater	16S rRNA sequencing	Attached to BC: Aminobacterium Syntrophomonas Sporanaerobacter Escherichia	Attached to BC: Methanobacterium Methanosarcina Methanobrevibacter	[53]
Sawdust	500	248 ± 34	-	-	55	Food waste	16S rRNA sequencing	Coprothermobacter (36.3%) Fervidobacterium (20.0%) Syntrophothermus Treponema	Methanosaeta (43.9%) Methanosarcina (15.8%)	[46]
Corn stover	850	315.2	-	0.09	55	Primary sludge + WAS	16S rRNA sequencing	Firmicutes (Clostridia) Bacteroidetes Proteobacteria	Methanothermobacter (>90%) Methanosarcina	[34]
Pine		353.1	-	0.23						
Sawdust	500	248.6 ± 9.4	0.11 μS cm^{-1}	-	55	Food waste + Sewage sludge	16S rRNA sequencing	Defluviitoga Tepidimicrobium	Methanothermobacter Methanosarcina	[49]

NA: not available; CLSM: confocal laser scanning microscopy; FISH: Fluorescence in situ hybridization; OFMSW: organic fraction of municipal solid waste; SSA: surface area; WAS: waste activated sludge.

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4.4. Effect of biochar on digestate quality

Anaerobic digestate has been considered as soil improver because it is rich in nutrients [184–186]. However, challenges related to digestate management have recently grown in association with EU regulations on ammonia, volatile organic acids, phenolic compounds, heavy metals, PAHs and PCBs [4,187]. So far, most technologies available to exploit digestate as soil improver are based on mechanical/physical (e.g. mechanical dewatering, semipermeable membranes and evaporation) or chemical processes (e.g. ammonia stripping and nutrients adjustment) (Table 8).

Table 8. Advantages and disadvantages of conventional technologies for digestate processing [188–191].

Methods	Advantages	Disadvantages
Solid-liquid separation	Rich in phosphorus and suitable for fertilizer application	Liquid fraction has been considered as a surface and ground water pollutions
Belt and drum dryers	treatment and upgrading of digestate to a solid or concentrated product	Rapid volatilization of ammonium causes severe ammonia emission
High-Tech technologies (e.g. ammonia stripping, membrane process and vacuum evaporation exist)	Production of several streams with different physical and chemical properties.	Expensive
Mixing solid digestate with desired nutrient	Increasing value per ton	-

Dehydrated digestate could be used in non-agricultural markets as a heating fuel, however, this use implies nutrient and metal losses, which in turn have negative impacts

731 on the environment and crops. Consequently, three approaches have been conventionally
732 applied to reduce diffuse pollution resulting from digestate application to land [19,188]:
733 - Nutrient recovery from digestate;
734 - Carbon to Nitrogen ratio adjustment;
735 - Increasing of nutrient retention capacity using an additive.
736 One of the key aspects that should be considered when supplying additives to AD process
737 is their effects on the quality of digestate for subsequent uses, especially as soil improver.
738 Despite literature has not explored enough the fate and properties of digestate with BC to
739 land applications, some potential benefits of BC amendment can be identified as follows.
740 BC remaining in digestate after AD acts as a nutrient retention improver and catalyst,
741 mitigates leaching of heavy metals and pollutants via physical and chemical absorption
742 of organics, phosphate, ammonium, nitrate, nitrite, metals and CO_2 [19,192]. The
743 improvements on digestate quality can be related to BC features as SSA, surface
744 functional groups, ash content and presence of metals (Table 9).
745
746 Table 9. Biochar properties able to improve digestate quality

Factors	Function	Literature	Reference
Textural properties (surface area, pore size)	Higher content of functional group (e.g. Si–O–Si, O–H and C=O)	HCl, $NH_3 \cdot H_2O$ and $KMnO_4$ modification were performed to obtain functional biochar from Swine manure digestate.	[193]
	Increase of the pH and cation exchange capacity	H_2O_2 and KOH modification were performed to obtain functional biochar from domestic sewage sludge digestate	[104]
Ash content	Alkali and alkaline earth metals increase the alkalinity	Pinewood and white oak biochars made digestate a great alternative to agricultural lime fertilizer.	[33]

Metals on the surface	The cation form of the metal can bind with soluble phosphorus	Ex: $3Fe(OH)_2 + 2H_3PO_4^{3-} \rightarrow Fe_3(PO_4)_2 + 6H_2O$	[151]
Functional group	Negatively charged functional groups forms complexes with heavy metals	Manganese oxide-modified biochar composite derived from corn straws improved heavy metal stabilization in the digestate	[194]

747

748 BC supplement in digesters may be beneficial to the fertilizer value of digestates. Shen et
749 al. [34,151] have found that BC addition can cause a substantial increase of the macro-
750 and micro-nutrients as N, P, K, Ca, Mg, and Fe in digestate. Zhang et al. (2020) [195]
751 reported a similar rise of nutrient content in digestate amended with BC, even if
752 concentrations of certain nutrients did not fully meet limits of EU regulation on fertilizing
753 products (Regulation EU 2019/1009). Research has shown that the joint amendment of
754 BC and anaerobic digestate can reduce atmospheric greenhouses emissions from fields,
755 such as N_2O [196] and CO_2 [197–199]. A mixture of dried anaerobic digestate and BC
756 may be an alternative to standard formulations in horticultural potting media [200]. In
757 addition, BC may contribute to improve the composting of digestate [153,201,202],
758 particularly in terms of process performance, compost quality and its benefits on plants
759 [203–205].
760 Further research is needed to understand interactions between BC, digestate and soil for
761 the potential use of the mixture as soil improver after AD. Future studies about the use of
762 BC as additive in AD should also consider its effects on the agronomic value of anaerobic
763 sludge (i.e. content in macro- and micro-nutrients, germination and phytotoxicity tests,
764 and others [206]).

765 *4.5. Effects on biogas upgrading*

766 Raw biogas from AD consists mainly of CH_4 (50-70 % v/v) and CO_2 (30-50 % v/v), along
767 with minor compounds as water vapour, H_2S, NH_3, O_2 and N_2 [207]. Upgrading and
768 cleaning biogas are required to meet the requirements and standards for engines and
769 pipelines, although they represent energetic and economic costs up to 55 % of the total
770 biomethane production cost [33,208,209]. To date, conventional technologies involve
771 water scrubbing, cryogenic separation, physico-chemical absorption, and membranes,
772 among the others [210,211]. Recently, BC has been investigated as adsorbent of CO_2 and
773 H_2S for in-situ and ex-situ applications, as addressed in the following paragraphs.

774 *4.5.1. In-situ biogas upgrading*

775 A series of studies [24,33,34,151] investigated the feasibility of in-situ biogas upgrading
776 by the addition of BC, obtaining methane contents up to pipeline quality (Table 10). Shen
777 et al. (2015) [151] investigated the possibility of sequestering CO_2 with BC during
778 thermophilic AD of WAS for in-situ biogas cleaning and upgrading. They reported
779 average methane contents of 88.5-96.7 % in BC amended reactors, compared to 67.9 %
780 in control reactor, reaching CO_2 removals of 54.9-86.3 % and residual H_2S content below
781 5 ppb. They suggested that CO_2 removal could be promoted by the high porosity of BC,
782 by the large SSA rich of basic sites and of hydrophobic sites. Shen et al. (2016) [33]
783 assessed the AD of WAS with the addition of two woody BCs. They observed average
784 methane content up to 92.3 % and 79.0 % in biogas from BCs amended reactors in
785 mesophilic and thermophilic conditions compared to control reactors, corresponding to
786 CO_2 removals by up to 66.2 % and 32.4 %, respectively. They stated that both BCs owned
787 desirable properties for CO_2 sequestration, and in particular high values of: SSA, porosity,

788 chemical stability, degree of carbonization and alkaline nature. Linville et al. (2017) [24]
789 investigated the influence of particle size and dose of BC from walnut shell on AD of FW
790 in mesophilic and thermophilic conditions. They found higher CO_2 removals compared
791 to control reactors in the case of smaller particle size of BC (61.0 %) than coarse one
792 (51.0 %), due to the larger SSA and ash content. However, according to other studies
793 [33,151], they observed a reduction of methane production with higher BC doses,
794 concluding that this could lead to inhibition caused by higher concentrations of cations
795 released by the BC. Shen et al. (2017) [34] studied the effects of two BCs from corn stover
796 and pine wood on AD of WAS in two-stage digesters. They reported an average methane
797 content of 81.0-88.6 % in the reactor with BC from corn stover and 72.1-76.6 % with BC
798 from pine wood, compared to around 70.0 % for the control. They stated that BCs would
799 release base cations sequestrating CO_2 by chemical sorption and forming
800 bicarbonate/carbonate salts, and that its surface structure would help CO_2 adsorption.
801 Apart from CO_2 adsorption on BC, the major formation of CH_4 depends on the stronger
802 syntrophic cooperation between organic acid-oxidising bacteria and CO_2 reducing
803 methanogens [36,58], underlying the key role of efficient interspecies electron transfers.
804 Further confirmation by other authors to the attractive findings about biogas in-situ
805 upgrading by BC would be beneficial.

806 *4.5.2. Ex-situ biogas cleaning and upgrading*

807 The use of BC and other carbonaceous adsorbents for CO_2 capture from various gaseous
808 streams recently attracted a growing attention [212–214]. Considering ex-situ
809 applications of BC for biogas upgrading and cleaning, Table 11 shows CO_2 and H_2S
810 adsorption capacity of different BCs. Clearly, the adsorption capacity for both CO_2 and
811 H_2S is in a wide range, 0.4-2.3 mmol g^{-1} and 0.2-19.1 mmol g^{-1} respectively. Most of the

812 studies regarding CO_2 capture do not specifically focus on biogas, investigating different
813 BCs eventually subjected to activation. Sethupathi et al. (2017) [215] assessed the
814 adsorption of CH_4, CO_2 and H_2S in a synthetic biogas stream by four BCs in fixed bed
815 adsorbers during continuous experiments. They reported that just CO_2 and H_2S were
816 captured by BCs, which exhibited adsorption capacities up to 0.208 mmol g^{-1} for H_2S and
817 0.126 mmol g^{-1} for CO_2. Creamer et al. (2014) [216] investigated the adsorption of CO_2
818 into BCs from bagasse and hickory wood. They found that BC could effectively capture
819 CO_2 (adsorption capacity up to 73.55 mg g^{-1} or 1.67 mmol g^{-1}), suggesting the importance
820 of surface area and superficial nitrogen groups in CO_2 sequestration, mainly through
821 physical adsorption. Creamer and Gao (2016) [217] reported that the main mechanism
822 for CO_2 sequestration by BC is physical adsorption, suggesting the importance of high
823 SSA [100], adequate pore size (0.5-0.8 nm) [218] and pore volume, thanks to Van der
824 Waals and electrostatic forces. However, the adsorption of CO_2 can also be influenced by
825 BC chemical properties, such as the presence of basic surface functional groups or alkali
826 and alkaline earth metals, hydrophobicity and non-polarity [214]. For instance, Xu et al.
827 (2016) [219] found that the adsorption of CO_2 by three BCs during batch equilibrium tests
828 was due to the presence of alkali and alkaline earth metals (Ca, Fe, K, Mg) by CO_2
829 mineralogical reactions together with physical sorption. Activation and surface treatments
830 of BCs can provide high surface area and micropores for physical sorption and enrich
831 surface functional groups and metal oxides for chemical sorption, leading to remarkable
832 CO_2 adsorption capacities (5.0-7.4 mmol g^{-1}) [220].
833 Other studies applied BC for removing H_2S from biogas (Table 11). Sahota et al. 2018
834 [221] found 84.2 % removal of H_2S from biogas with BC from leaf waste. Kanjanarong
835 et al. (2017) [222] obtained a removal of 98 % of H_2S (8.02 mmol g^{-1}) from biogas with

836 BC, suggesting carboxylic and hydroxide radical groups as responsible of H_2S adsorption.
837 Finally, Pelaez-Samaniego et al. (2018) [37] found that BC from AD digestate could
838 effectively remove H_2S from a synthetic biogas, possibly facilitated by the presence of
839 ash, porosity, or aromatics in BC. In contrast with CO_2 for which adsorption onto BC
840 seemed to be mainly physical, absorption of H_2S seemed to involve many chemical
841 mechanisms with BC surface [223].
842 Overall, biochar seems to be a promising adsorbent for ex-situ biogas cleaning and
843 upgrading applications. However, additional studies [215] should focus on the adsorption
844 of CO_2 and H_2S along with NH_3 from real or synthetic biogas, considering their
845 competitive adsorptions, along with the influence of water vapour and the eventual
846 removal of CH_4.
847
848 Table 10. Physic-chemical properties of biochars used in biogas in-situ upgrading

Feedstock	Production temperature [°C]	BET-SA [m^2g^{-1}]	Total pore volume [cm^3g^{-1}]	Average pore diameter [nm]	H/C [molar ratio]	O/C [molar ratio]	Ash [% wt]	Reference
Corn stover	Gasification	315.30	0.09	6.50	0.075 ± 0.007	0.004 ± 0.001	45.18 ± 0.40	[34,151]
Pine pellets	Gasification	310.19	0.19	5.07	0.078 ± 0.009	0.249 ± 0.014	18.69 ± 0.44	[33,34]
White oak pellets	Gasification	296.81	0.15	4.92	0.109 ± 0.026	0.051 ± 0.010	34.90 ± 0.65	
Walnut shell	Gasification: 900 °C	86.5	0.16	7.06	0.20 ± 0.01	0.06 ± 0.01	43.2 ± 0.2	[24]

849
850 Table 11. Biochar adsorption capacity (mmol g^{-1}) of H_2S and CO_2 during ex-situ
851 applications.

Feedstock	Pyrolysis/activation	Surface area [m^2g^{-1}]	Total pore volume [cm^3g^{-1}]	Gas	Inlet H_2S or CO_2 concentration [ppm]	H_2S Adsorption capacity [mmol g^{-1}]	CO_2 Adsorption capacity [mmol g^{-1}]	Reference

AD digestate fibres	PY/500°C/60 min	134	0.037	Synthetic biogas	2000	3.96 [a]		[37]
	PY/600°C/60min	142	0.035	Synthetic biogas	2000	15.90 [a]		
	PY/600°C/60min +Na_2CO_3	-	-	Synthetic biogas	2000	19.13 [a]		
Biomass from black liquor	C/450°C/6min	60		N_2+H_2S	1000	2.14 [a]		[224]
Pig manure	PY/500°C/4hours	47.4		Air + H_2S	1% (v/v)	1.75 [a]		[225]
Sewage sludge	PY/500°C/4hours	71.6		Air + H_2S	1% (v/v)	1.29 [a]		
Potato peel waste	C/500°C/5min	63		N_2 + H_2S	1000	1.56 [a]		[226]
Camphor	PY/400°C/5hours	20				3.21 [a]		[227]
Rice hull	PY/400°C/5hours	115				11.23 [a]		
Bamboo	PY/400°C/5hours	58				9.88 [a]		
80% wood chips 20% AD digestate	PY/600°C			Biogas	1020	8.02 [a]		[222]
Perilla leaf	PY/700°C	473.4	0.1	Synthetic biogas		0.537	2.312	[215]
Korean oak	PY/400°C	270.8	0.1	Synthetic biogas		0.178	0.597	
Japanese oak	PY/500°C	475.6	0.2	Synthetic biogas		0.167	0.379	
Soybean stover	PY/700°C	420.3	0.2	Synthetic biogas		0.308	0.707	
Sawdust	G/850°C	182.04	0.0036	N_2/CO_2			1.08 [b]	[228]
	G/850°C + monoethanolamine	3.17	0.0070	N_2/CO_2			1.02 [b]	
Sugarcane bagasse	PY/600°C	401.00					1.67 [b]	[216]
Whitewood	PY/500°C + steam activation	840	0.55	He/CO_2	30 % mol		1.34 [b]	[229]
Whitewood	PY/500°C + CO_2 activation	820	0.45	He/CO_2	30 % mol		1.43 [b]	
Whitewood	PY/500°C + KOH activation	1400	0.62	He/CO_2	30 % mol		1.77 [b]	
Walnut shell	C900°C/1.5hours	397	0.198				1.65 [b]	[230]
Pig manure	PY/500°C/4hours	31.57	0.044	N_2/CO_2			0.53 [b]	[219]
Wheat straw	PY/500°C/4hours	20.20	0.041	N_2/CO_2			0.78 [b]	
Sewage sludge	PY/500°C/4hours	10.12	0.022	N_2/CO_2			0.41 [b]	

5. Economic and environmental assessments

An economic and environmental evaluation of BC production and application in AD was performed, considering specifically four perspectives: 1. BC production according to feedstock composition and 2. to pyrolysis process conditions; 3. BC application in AD compared to current state of the art technologies addressing AD challenges; 4. integration of AD and pyrolysis processes (to our knowledge, specific studies related to the economic and environmental assessment of BC use in AD processes are not available).

5.1. Economic assessment

Considering BC production, the key parameters to evaluate the economic benefits of feedstocks (perspective 1) are: ash and lignin contents and O/C ratio, which affect pyrolysis yield, molecular weight of bio-oil and BC amount production [231]. Li et al. (2017) [232], based on regression model applied to 346 lignocellulosic feedstocks, stated that higher ash content increases BC production in a range of 12.5-15.5 %, reducing bio-oil production, and consequently the incomes coming out from bio-oil trade, which makes pyrolysis economically profitable. With lower ash content and higher O/C ratio of feedstocks, higher biofuel yields are produced, which leads to better economic performance, in fact minimum fuel selling prices for lignocellulosic feedstocks ranged from 0.53-1.1 Euro/L.

Considering the pyrolysis process (perspective 2), the investment costs for BC production from lignocellulosic feedstocks are: 43 % for pre-treatment and pyrolysis, 35 % for H_2 generation and 22 % for cooling and fractionations [232]. The average operating cost varies from 0.68 Euro/L for woody biomass to 0.86 Euro/L for straw biomass, due to the higher costs of disposal and pre-treatment of straw biomass, respectively 32 % and 34 %

875 of total operational costs [233]. Based on the economic analysis performed by Harsono
876 et al. (2013) [234] and Sahoo et al. (2019) [235], the investment and operational costs
877 related to BC production from lignocellulosic feedstock can only be balanced by a BC
878 trade price of 470 Euro/t.
879 Considering perspective 3, the need to enhance AD feasibility and applicability to
880 unconventional substrates implied higher costs, which should be exceeded by the
881 increased methane production and therefore by the additional electric energy potentially
882 associated. Inorganic and biological additives as iron, micronutrients and ash are
883 conventionally employed to reduce inhibition and facilitate organic matter solubilisation,
884 thus improving methane production. Nevertheless, the application of additives in AD
885 accounts as 3.60-4.10 euro/L of enzyme and as 13-16 euro/L of nutrients [236]. The
886 overall costs of BC, depending on feedstock, pyrolysis process and activating agent
887 (Table 12), could range from 0.2 to 0.5 USD/kg, making BC cheaper than granular
888 activated carbon (GAC), which has production costs ranging between 0.6 and 20 USD/kg.
889
890 Table 12. Comparison of granular activated carbon (GAC) and biochar (BC) production
891 costs depending on feedstock, production process and activating agent

Additive	Feedstock	Production process/ Activating agent	Location	Cost of production (USD kg^{-1})	Reference
GAC	Poultry litter derived carbon	Steam	USA	1.44	[237]
GAC	Rice bran	NaOH	China	3.58-3.77	[237]
GAC	Red oak wood	Steam	USA	0.62-1.27	[237]
GAC - commercial	-	-	USA	1.19-16.34	[237]
GAC	Fruit processing waste	Steam	Malaysia	1.67	[237]
GAC	Rice bran	CO_2	Brazil	3.54	[237]

GAC	Acid treated rice bran	CO_2	Brazil	20.45	[237]
GAC	Wood	KOH	-	2.49	[237]
GAC	Charcoal	KOH	-	1.25	[237]
GAC	Lignite	KOH	-	2.18	[237]
GAC - commercial				1.93	[237]
BC	Empty fruit bunches	Slow PY	Malaysia	0.533	[234]
BC	Straw	Slow PY (large scale)	UK	0.203	[18]
BC	Straw	Slow PY (medium scale)	UK	0.447	[18]
BC	Straw	Slow PY (small scale)	UK	0.351	[18]
BC	Short rotation coppicing, forestry residues, short rotation forestry	Slow PY (large scale)	UK	0.266	[18]
BC	Short rotation coppicing, forestry residues, short rotation forestry	Slow PY (medium scale)	UK	0.500	[18]
BC	Short rotation coppicing	Slow PY (small scale)	UK	0.434	[18]
BC	Forestry residue	Slow PY (large scale)	UK	0.345	[18]
BC	Forestry residue	Slow PY (medium scale)	UK	0.584	[18]
BC	Arboricultural arisings	Slow PY (small scale)	UK	0.213	[18]
BC	Pine wood	Slow PY	USA	0.220-0.280	[238]
BC	-	-	European market (2014)	0.662-0.811[a]	[239]
BC	-	-	-	0.207	[239]
BC	-	-	-	0.600	[68]
BC	-	-	Global, market price (mean)	2.06	[240]
BC	-	-	USA, market price (mean)	2.48 (0.08-13.48)	[241]

GAC: granular activated carbon; PY: pyrolysis.
(a) exchange rate USD/euro (January 2014): 1.3516

892

893 Still considering perspective 3 and moving from the additive's cost to the improvement
894 of AD performances,
895 The economic benefits of the integration of AD and pyrolysis technologies (perspective
896 4) has been explored by literature. The integrated technologies of AD of waste biomass
897 and pyrolysis of the digestate could increase the net electricity production respect to AD
898 alone [80] and enhance its quality as soil amendment [81] with economic and
899 environmental benefits [242]. However, up to date, there is uncertainty regarding the
900 balance between input costs of BC supplementation and output of energy production from
901 AD. Qiu et al. (2019) [59] proposed the energy input-output LCA method to estimate the
902 total energy input for biogas production, by calculating the energy associated with each
903 component used in AD, and the actual energy return of investment. Zhang et al. (2020)
904 [243] investigated the addition of woody BC to improve the thermophilic AD of FW.
905 They concluded that BC supplementation could be economically feasible to enhance
906 thermophilic AD of FW.

907 *5.2. Environmental assessment*

908 Considering feedstocks (perspective 1), life cycle analysis (LCA) from cradle to cradle
909 of the pyrolysis of lignocellulosic feedstocks stated that GHG emissions for husk/shell/pit
910 ranged from 120-250 g CO_2eq/MJ, while for other organic waste, wood and straw they
911 ranged between 20-50 g CO_2eq/MJ [232]. This difference was due to the dominant
912 contribution of indirect land use change from food production. Feedstocks having higher
913 O/C ratio and 0 – 2 % ash content increased the GHG emissions [244]. Based on GREET
914 database [245], GHG emissions reduction for lignocellulosic feedstocks was 85 - 98 %
915 compared to the GHG emissions for petroleum fuels refining, which was equal to 93

916 gCO_2eq/MJ. GHG emission reductions for lignocellulosic feedstocks satisfy the 50 %
917 share of renewable fuel standard for GHG emission reduction requirement for advanced
918 fuels [246].
919 Considering BC production process (perspective 2), LCA from cradle to gate showed that
920 BC produced from palm oil empty fruit bunches through slow pyrolysis had an energy
921 content higher than the energy required for producing BC [234]. Furthermore, LCA
922 cradle-to grave proved the positive energy balance of BC produced from different
923 lignocellulosic materials [247]. Hence, the positive energy balance of BC production and
924 application, due to the high-energy content of lignocellulosic feedstocks, represents a
925 crucial benefit both from economic and environmental perspectives. One of the main
926 issue of BC produced from renewable feedstocks as lignocellulose wastes (i.e. WAS,
927 wood) and not from purpose grown feedstocks is the higher risk of having contaminants
928 as heavy metals or organic compounds like dioxins, PAHs and PCBs [248].
929 Still considering BC process production (perspective 2), pyrolysis and gasification were
930 compared from the perspective of carbon equivalent abatement (CA): pyrolysis achieved
931 the highest CA, ranging from 0.07 to 1.25 t CO_2 eq/t feedstock, as cardboard and wood
932 waste, while gasification reached the highest electricity generation outputs with 0.9
933 MWhe/t of feedstocks [249]. Activation was proven to represent a high item cost both in
934 terms of economic and environmental perspectives [250]. BC chemical activation costs,
935 in line with non-renewable GAC activation, range between 1.38 and 1.48 Euro/kg,
936 respectively with acidic and basic treatments [251].
937 However, perspective 2 could also be explored considering the existing literature related
938 to the conventional applications of BC as soil improver, adsorbent for water and air
939 pollutants, catalyst for syngas upgrading and biodiesel production (Table 13). LCA

940 studies from cradle-to-grave of conventional BC applications measured in all cases
941 positive environmental benefits compared to conventional perspectives. BC produced
942 from waste forestry feedstock and applied as soil improver contributed to GHGs emission
943 reduction up to 2.74 kg CO_2 eq/ kg BC for the impact categories climate change (CC),
944 natural gas avoided for fossil depletion (FD) and urea avoided for freshwater
945 eutrophication (FE) and human toxicity (HT) [252]. A LCA from cradle to cradle [247]
946 showed that BC production and application as adsorbent presented, compared to GAC
947 deriving from virgin non-renewable feedstock, lower environmental impacts in terms of
948 climate change (CC), fossil depletion (FD), freshwater eutrophication (FE) and terrestrial
949 acidification (TA) impact categories, and that wood and wood chips achieved the highest
950 environmental credits among the others feedstocks. In details, considering CC (expressed
951 as kg CO_2/kg adsorption material), GAC produced 1.44, while wood chips and corn stover
952 had credits ranging between -3.42 to -3.57, whereas oil palm produced 11.1 [253].
953 Regarding FE (evaluated as kg P eq/ kg adsorption material), BC from lignocellulosic
954 feedstock exhibited higher values than GAC, respectively ranging between 6.2 to 10.9 %
955 [247], due to the organic matter of renewable feedstock [254]. Considering both TA and
956 FD (respectively estimated as kg SO_2 eq/ kg adsorption material and kg oil eq/ kg
957 adsorption material), BC from lignocellulosic feedstock achieved higher credits than
958 GAC, between 9.5 % and 32.0 %.
959 Considering BC application in AD processes (perspective 3), to our knowledge the
960 available scientific literature only focused on sequential processes, as pyrolysis followed
961 by AD. A LCA from cradle to grave [255] considered BC produced from corn stover
962 applied as carburant and soil amendment with sequential AD, achieving respectively: -

963 2.47 kg CO_2eq/t and energy saving of -6.53 MJ/ t for the first scenario and - 4.67 kg

964 CO_2eq/t and energy saving of -9.73 MJ/ t for the second scenario.

965

966 Table 13. Environmental assessment of biochar (BC) production and uses

	Positive effects	Negative effects
Feedstock (perspective 1)	Lignocellulosic biomass exhibited more positive effects because of higher energy potential [247] Waste biomasses presented more advantages (e.g. avoided waste management) [256]	Feedstock provision (transport) [93] Potential presence of contaminants (heavy metals, persistent organic pollutants) in waste feedstocks (sewage sludge) [256]
Production process (perspective 2)	Renewable energy from syngas and bio-oil [93] Stabilization of C in biomass feedstock [18]	Large centralized pyrolysis units higher transportation distances compared to smaller decentralized units [256]
Activation process (perspective 2)		Activation was proven to represent a high item cost both in terms of economic and environmental perspectives [250]. Use of chemicals and electricity is associated to higher impacts [257].
Applications		
Soil improver	Biochar (C) sequestration in the soil [93] Reduced fertiliser requirements [93] Reduced N_2O emissions from soil [93] Enhanced plants growth [18] Reduced fossil fuel use in irrigation and cultivation [18] Enhanced nutrient availability [258] Increased H_2O retention [258] Reduced leaching and run-off of nutrients [258]	Binding /deactivation of pesticides, herbicides and nutrients in soil [258] BC as source of potential toxicants (heavy metals, PAHs, organics) [258]
Adsorbent	BC lower impacts than activated carbon [247]	

967

968

969 In conclusion, focusing the environmental assessment on perspective 4, the integration of

970 AD of waste biomass and pyrolysis of digestate, as shown in Figure 2, could increase the

971 net electricity production respect to AD alone [80] and enhance its quality as soil
972 amendment [81] with economic and environmental benefits [242]. In conclusion, the
973 integrated approach has been investigated by life cycle analysis and exhibited positive
974 environmental outcomes if compared with non-integrated processes [255,259].

975 **6. Conclusions**

976 This review addressed three key issues related to the comprehension of BC role in AD
977 processes:

978 *1. Investigation of the influence of BC properties on AD performances and of their ability*
979 *to counteract its main challenges*. It is understood that BC properties are determined
980 by the feedstock and by pyrolysis and activation processes. The key features were
981 SSA, porous structure and distribution, nature of surface functional groups (related to
982 CEC and adsorption capacity, buffer capacity, ability to immobilize microbial
983 communities), elemental composition and ash content. However, some mechanisms
984 (e.g. BC role in ammonium adsorption and BC influence on microbial mechanisms)
985 still need to be fully understood and explained. Other challenges for future research
986 are related to digestate management; in detail, the influence of BC relatively high doses
987 on the rheological properties of the digestate should be explored, as well as the
988 eventual leaching of pollutants in the environment as a consequence of digestate
989 recovery as soil improver.

990 *2. Assessment of the optimal BC production chain (i.e. feedstock-pyrolysis-activation) to*
991 *achieve the desired features*. Lignocellulosic biomasses, slow pyrolysis and physical
992 activation seemed to be a good combination in general, while other feedstocks and/or
993 chemical activation should be evaluated for specific needs and tailor-made applications.

However, a systematic investigation of the correlations linking BC physico-chemical characteristics and AD performances, carefully exploring one by one the BC effects mentioned in this review, is highly needed for a deep understanding of BC role as additive in AD processes.

3. Evaluation of the economic and environmental advantages connected to BC use in AD processes, compared to conventional solutions applied to address AD challenges. The main research gap related to this issue is the absence of specific literature related to BC use in AD processes, therefore only general statements could be formulated. The use of BC as additive could be cheaper and has less environmental impacts than of conventional AD improvers (e.g. physico-chemical-biological pre-treatments) and of GAC. The integration of AD and pyrolysis achieved economic feasibility and positive environmental performances if compared with non-integrated processes. Future research could investigate the optimization of technical, economic and environmental performances of BC production chain and its integration in AD processes.

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References

[1] Enerdata. World Energy Consumption Statistics. Glob Energy Stat Yearb 2019.

https://yearbook.enerdata.net/total-energy/world-consumption-statistics.html (accessed April 28, 2020).

[2] International Energy Agency (IEA). Statistics | World - Total Primary Energy Supply (TPES) by source 2018. https://www.iea.org/statistics/?country=WORLD&year=2016&category=Energy supply&indicator=TPESbySource&mode=chart&dataTable=BALANCES (accessed February 25, 2019).

[3] Weiland P. Biogas production: current state and perspectives. Appl Microbiol Biotechnol 2010;85:849–60. doi:10.1007/s00253-009-2246-7.

[4] Nkoa R. Agricultural benefits and environmental risks of soil fertilization with anaerobic digestates: a review. Agron Sustain Dev 2014;34:473–92. doi:10.1007/s13593-013-0196-z.

[5] Walsh JJ, Jones DL, Edwards-Jones G, Williams AP. Replacing inorganic fertilizer with anaerobic digestate may maintain agricultural productivity at less environmental cost. J Plant Nutr Soil Sci 2012;175:840–5. doi:10.1002/jpln.201200214.

[6] Ward AJ, Hobbs PJ, Holliman PJ, Jones DL. Optimisation of the anaerobic digestion of agricultural resources. Bioresour Technol 2008;99:7928–40. doi:10.1016/J.BIORTECH.2008.02.044.

[7] Appels L, Lauwers J, Degrève J, Helsen L, Lievens B, Willems K, et al. Anaerobic digestion in global bio-energy production: Potential and research challenges. Renew Sustain Energy Rev 2011;15:4295–301. doi:10.1016/J.RSER.2011.07.121.

[8] European Biogas Association (EBA). Statistical report, 2019 2019.

https://www.europeanbiogas.eu/eba-statistical-report-2019 (accessed May 8, 2020).

[9] Mata-Alvarez J, Dosta J, Romero-Güiza MS, Fonoll X, Peces M, Astals S. A critical review on anaerobic co-digestion achievements between 2010 and 2013. Renew Sustain Energy Rev 2014;36:412–27. doi:10.1016/J.RSER.2014.04.039.

[10] Taherzadeh M, Karimi K, Taherzadeh MJ, Karimi K. Pretreatment of Lignocellulosic Wastes to Improve Ethanol and Biogas Production: A Review. Int J Mol Sci 2008;9:1621–51. doi:10.3390/ijms9091621.

[11] Carrere H, Antonopoulou G, Affes R, Passos F, Battimelli A, Lyberatos G, et al. Review of feedstock pretreatment strategies for improved anaerobic digestion: From lab-scale research to full-scale application. Bioresour Technol 2016;199:386–97. doi:10.1016/j.biortech.2015.09.007.

[12] Arif S, Liaquat R, Adil M. Applications of materials as additives in anaerobic digestion technology. Renew Sustain Energy Rev 2018;97:354–66. doi:10.1016/j.rser.2018.08.039.

[13] Ye M, Liu J, Ma C, Li Y-Y, Zou L, Qian G, et al. Improving the stability and efficiency of anaerobic digestion of food waste using additives: A critical review. J Clean Prod 2018;192:316–26. doi:10.1016/J.JCLEPRO.2018.04.244.

[14] Romero-Güiza MS, Vila J, Mata-Alvarez J, Chimenos JM, Astals S. The role of additives on anaerobic digestion: A review. Renew Sustain Energy Rev 2016;58:1486–99. doi:10.1016/j.rser.2015.12.094.

[15] González J, Sánchez M, Gómez X. Enhancing Anaerobic Digestion: The Effect of Carbon Conductive Materials. J Carbon Res 2018;4:59. doi:10.3390/c4040059.

[16] Zhang J, Zhao W, Zhang H, Wang Z, Fan C, Zang L. Recent achievements in enhancing anaerobic digestion with carbon- based functional materials. Bioresour Technol 2018;266:555–67. doi:10.1016/j.biortech.2018.07.076.

[17] Nanda S, Dalai AK, Berruti F, Kozinski JA. Biochar as an Exceptional Bioresource for Energy, Agronomy, Carbon Sequestration, Activated Carbon and Specialty Materials. Waste and Biomass Valorization 2016;7:201–35. doi:10.1007/s12649-015-9459-z.

[18] Lehmann J, Joseph S. Biochar for environmental management: science, technology and implementation. II. Earthscan from Routledge; 2015.

[19] Fagbohungbe MO, Herbert BMJ, Hurst L, Ibeto CN, Li H, Usmani SQ, et al. The challenges of anaerobic digestion and the role of biochar in optimizing anaerobic digestion. Waste Manag 2017;61:236–49. doi:10.1016/j.wasman.2016.11.028.

[20] Pecchi M, Baratieri M. Coupling anaerobic digestion with gasification, pyrolysis or hydrothermal carbonization: A review. Renew Sustain Energy Rev 2019. doi:10.1016/j.rser.2019.02.003.

[21] Fabbri D, Torri C. Linking pyrolysis and anaerobic digestion (Py-AD) for the conversion of lignocellulosic biomass. Curr Opin Biotechnol 2016;38:167–73. doi:10.1016/j.copbio.2016.02.004.

[22] Hübner T, Mumme J. Integration of pyrolysis and anaerobic digestion - Use of aqueous liquor from digestate pyrolysis for biogas production. Bioresour Technol 2015;183:86–92. doi:10.1016/j.biortech.2015.02.037.

[23] Salman CA, Schwede S, Thorin E, Yan J. Enhancing biomethane production by integrating pyrolysis and anaerobic digestion processes. Appl Energy 2017;204:1074–83. doi:10.1016/j.apenergy.2017.05.006.

[24] Linville JL, Shen Y, Ignacio-de Leon PA, Schoene RP, Urgun-Demirtas M. In-situ biogas upgrading during anaerobic digestion of food waste amended with walnut shell biochar at bench scale. Waste Manag Res 2017;35:669–79. doi:10.1177/0734242X17704716.

[25] Torri C, Fabbri D. Biochar enables anaerobic digestion of aqueous phase from intermediate pyrolysis of biomass. Bioresour Technol 2014;172:335–41. doi:10.1016/j.biortech.2014.09.021.

[26] Sunyoto NMS, Zhu M, Zhang Z, Zhang D. Effect of biochar addition on hydrogen and methane production in two-phase anaerobic digestion of aqueous carbohydrates food waste. Bioresour Technol 2016;219:29–36. doi:10.1016/j.biortech.2016.07.089.

[27] Jang HM, Choi YK, Kan E. Effects of dairy manure-derived biochar on psychrophilic, mesophilic and thermophilic anaerobic digestions of dairy manure. Bioresour Technol 2018;250:927–31. doi:10.1016/j.biortech.2017.11.074.

[28] Sun C, Liu F, Song Z, Wang J, Li Y, Pan Y, et al. Feasibility of dry anaerobic digestion of beer lees for methane production and biochar enhanced performance at mesophilic and thermophilic temperature. Bioresour Technol 2019;276:65–73. doi:10.1016/J.BIORTECH.2018.12.105.

[29] Zhao Z, Zhang Y, Woodard TL, Nevin KP, Lovley DR. Enhancing syntrophic metabolism in up-flow anaerobic sludge blanket reactors with conductive carbon materials. Bioresour Technol 2015;191:140–5. doi:10.1016/j.biortech.2015.05.007.

[30] Inthapanya S, Preston TR, Leng RA. Biochar increases biogas production in a batch digester charged with cattle manure. Livest Res Rural Dev 2012;24.

[31] Inthapanya S, Preston TR. Biochar marginally increases biogas production but decreases methane content of the gas in continuous-flow biodigesters charged with cattle manure. Livest Res Rural Dev 2013;25.

[32] Bruun EW, Müller-Stöver D, Ambus P, Hauggaard-Nielsen H. Application of biochar to soil and N2O emissions: potential effects of blending fast-pyrolysis biochar with anaerobically digested slurry. Eur J Soil Sci 2011;62:581–9. doi:10.1111/j.1365-2389.2011.01377.x.

[33] Shen Y, Linville JL, Ignacio-de Leon PAA, Schoene RP, Urgun-Demirtas M. Towards a sustainable paradigm of waste-to-energy process: Enhanced anaerobic digestion of sludge with woody biochar. J Clean Prod 2016;135:1054–64. doi:10.1016/j.jclepro.2016.06.144.

[34] Shen Y, Forrester S, Koval J, Urgun-Demirtas M. Yearlong semi-continuous operation of thermophilic two-stage anaerobic digesters amended with biochar for enhanced biomethane production. J Clean Prod 2017;167:863–74. doi:10.1016/j.jclepro.2017.05.135.

[35] Codignole Luz F, Cordiner S, Manni A, Mulone V, Rocco V. Biochar characteristics and early applications in anaerobic digestion-a review. J Environ Chem Eng 2018;6:2892–909. doi:10.1016/j.jece.2018.04.015.

[36] Masebinu SO, Akinlabi ET, Muzenda E, Aboyade AO. A review of biochar properties and their roles in mitigating challenges with anaerobic digestion. Renew Sustain Energy Rev 2019;103:291–307. doi:10.1016/J.RSER.2018.12.048.

[37] Pelaez-Samaniego MR, Smith MW, Zhao Q, Garcia-Perez T, Frear C, Garcia-Perez M. Charcoal from anaerobically digested dairy fiber for removal of

1136 hydrogen sulfide within biogas. Waste Manag 2018;76:374–82.
1137 doi:10.1016/j.wasman.2018.03.011.
1138 [38] Wang G, Li Q, Gao X, Wang XC. Synergetic promotion of syntrophic methane
1139 production from anaerobic digestion of complex organic wastes by biochar:
1140 Performance and associated mechanisms. Bioresour Technol 2018;250:812–20.
1141 doi:10.1016/j.biortech.2017.12.004.
1142 [39] Wang D, Ai J, Shen F, Yang G, Zhang Y, Deng S, et al. Improving anaerobic
1143 digestion of easy-acidification substrates by promoting buffering capacity using
1144 biochar derived from vermicompost. Bioresour Technol 2017;227:286–96.
1145 doi:10.1016/j.biortech.2016.12.060.
1146 [40] Fagbohungbe MO, Herbert BMJ, Hurst L, Li H, Usmani SQ, Semple KT. Impact
1147 of biochar on the anaerobic digestion of citrus peel waste. Bioresour Technol
1148 2016;216:142–9. doi:10.1016/j.biortech.2016.04.106.
1149 [41] Mumme J, Srocke F, Heeg K, Werner M. Use of biochars in anaerobic digestion.
1150 Bioresour Technol 2014;164:189–97. doi:10.1016/j.biortech.2014.05.008.
1151 [42] Shanmugam SR, Adhikari S, Nam H, Kar Sajib S. Effect of bio-char on methane
1152 generation from glucose and aqueous phase of algae liquefaction using mixed
1153 anaerobic cultures. Biomass and Bioenergy 2018;108:479–86.
1154 doi:10.1016/j.biombioe.2017.10.034.
1155 [43] Su C, Zhao L, Liao L, Qin J, Lu Y, … QD-J of C, et al. Application of biochar in
1156 a CIC reactor to relieve ammonia nitrogen stress and promote microbial
1157 community during food waste treatment. J Clean Prod 2019;209:353–62.
1158 doi:10.1016/j.jclepro.2018.10.269.
1159 [44] Lü F, Luo C, Shao L, He P. Biochar alleviates combined stress of ammonium and

acids by firstly enriching Methanosaeta and then Methanosarcina. Water Res 2016;90:34–43. doi:10.1016/j.watres.2015.12.029.

[45] Cruz Viggi C, Simonetti S, Palma E, Pagliaccia P, Braguglia C, Fazi S, et al. Enhancing methane production from food waste fermentate using biochar: The added value of electrochemical testing in pre-selecting the most effective type of biochar. Biotechnol Biofuels 2017;10:1–13. doi:10.1186/s13068-017-0994-7.

[46] Li Q, Xu M, Wang G, Chen R, Qiao W, Wang X. Biochar assisted thermophilic co-digestion of food waste and waste activated sludge under high feedstock to seed sludge ratio in batch experiment. Bioresour Technol 2018;249:1009–16. doi:10.1016/j.biortech.2017.11.002.

[47] Martínez EJ, Rosas JG, Sotres A, Moran A, Cara J, Sánchez ME, et al. Codigestion of sludge and citrus peel wastes: Evaluating the effect of biochar addition on microbial communities. Biochem Eng J 2018;137:314–25. doi:10.1016/j.bej.2018.06.010.

[48] Luo C, Lü F, Shao L, He P. Application of eco-compatible biochar in anaerobic digestion to relieve acid stress and promote the selective colonization of functional microbes. Water Res 2015;68:710–8. doi:10.1016/j.watres.2014.10.052.

[49] Wang G, Li Q, Gao X, Wang XC. Sawdust-Derived Biochar Much Mitigates VFAs Accumulation and Improves Microbial Activities To Enhance Methane Production in Thermophilic Anaerobic Digestion. ACS Sustain Chem Eng 2019:acssuschemeng.8b04789. doi:10.1021/acssuschemeng.8b04789.

[50] Wang C, Liu Y, Gao X, Chen H, Xu X, Zhu L. Role of biochar in the granulation of anaerobic sludge and improvement of electron transfer characteristics.

1184 Bioresour Technol 2018;268:28–35. doi:10.1016/j.biortech.2018.07.116.
1185 [51] Zhao Z, Zhang Y, Holmes DE, Dang Y, Woodard TL, Nevin KP, et al. Potential
1186 enhancement of direct interspecies electron transfer for syntrophic metabolism of
1187 propionate and butyrate with biochar in up-flow anaerobic sludge blanket
1188 reactors. Bioresour Technol 2016;209:148–56.
1189 doi:10.1016/j.biortech.2016.03.005.
1190 [52] Yu HQ, Tay JH, Fang HHP. Effects of Added Powdered and Granular Activated
1191 Carbons on Start-Up Performance of UASB Reactors. Environ Technol
1192 1999;20:1095–101. doi:10.1080/09593332008616906.
1193 [53] Cooney MJ, Lewis K, Harris K, Zhang Q, Yan T. Start up performance of
1194 biochar packed bed anaerobic digesters. J Water Process Eng 2016;9:e7–13.
1195 doi:10.1016/j.jwpe.2014.12.004.
1196 [54] Dang Y, Sun D, Woodard TL, Wang LY, Nevin KP, Holmes DE. Stimulation of
1197 the anaerobic digestion of the dry organic fraction of municipal solid waste
1198 (OFMSW) with carbon-based conductive materials. Bioresour Technol
1199 2017;238:30–8. doi:10.1016/j.biortech.2017.04.021.
1200 [55] Sasaki K, Morita M, Hirano S, Sasaki D, Ohmura N, Igarashi Y. Efficient
1201 degradation of rice straw in the reactors packed by carbon fiber textiles. Appl
1202 Microbiol Biotechnol 2010;87:1579–86. doi:10.1007/s00253-010-2667-3.
1203 [56] Martins G, Salvador AF, Pereira L, Alves MM. Methane Production and
1204 Conductive Materials: A Critical Review. Environ Sci Technol 2018;52:10241–
1205 53. doi:10.1021/acs.est.8b01913.
1206 [57] Chen S, Rotaru AE, Shrestha PM, Malvankar NS, Liu F, Fan W, et al. Promoting
1207 interspecies electron transfer with biochar. Sci Rep 2014;4.

1208 doi:10.1038/srep05019.
1209 [58] Pan J, Ma J, Zhai L, Luo T, Mei Z, Liu H. Achievements of biochar application
1210 for enhanced anaerobic digestion: A review. Bioresour Technol
1211 2019;292:122058. doi:10.1016/j.biortech.2019.122058.
1212 [59] Qiu L, Deng YF, Wang F, Davaritouchaee M, Yao YQ. A review on biochar-
1213 mediated anaerobic digestion with enhanced methane recovery. Renew Sustain
1214 Energy Rev 2019;115:109373. doi:10.1016/J.RSER.2019.109373.
1215 [60] Nanda S, Azargohar R, Kozinski JA, Dalai AK. Characteristic Studies on the
1216 Pyrolysis Products from Hydrolyzed Canadian Lignocellulosic Feedstocks.
1217 BioEnergy Res 2014;7:174–91. doi:10.1007/s12155-013-9359-7.
1218 [61] Azargohar R, Nanda S, Kozinski JA, Dalai AK, Sutarto R. Effects of temperature
1219 on the physicochemical characteristics of fast pyrolysis bio-chars derived from
1220 Canadian waste biomass. Fuel 2014;125:90–100. doi:10.1016/j.fuel.2014.01.083.
1221 [62] Azargohar R, Nanda S, Rao BVSK, Dalai AK. Slow Pyrolysis of Deoiled Canola
1222 Meal: Product Yields and Characterization. Energy & Fuels 2013;27:5268–79.
1223 doi:10.1021/ef400941a.
1224 [63] Mohanty P, Nanda S, Pant KK, Naik S, Kozinski JA, Dalai AK. Evaluation of
1225 the physiochemical development of biochars obtained from pyrolysis of wheat
1226 straw, timothy grass and pinewood: Effects of heating rate. J Anal Appl Pyrolysis
1227 2013;104:485–93. doi:10.1016/j.jaap.2013.05.022.
1228 [64] Kan T, Strezov V, Evans TJ. Lignocellulosic biomass pyrolysis: A review of
1229 product properties and effects of pyrolysis parameters. Renew Sustain Energy
1230 Rev 2016;57:126–1140. doi:10.1016/j.rser.2015.12.185.
1231 [65] Garcia-Nunez JA, Pelaez-Samaniego MR, Garcia-Perez ME, Fonts I, Abrego J,

1232 Westerhof RJM, et al. Historical Developments of Pyrolysis Reactors: A Review.
1233 Energy and Fuels 2017;31:5751–75. doi:10.1021/acs.energyfuels.7b00641.
1234 [66] Bridgwater A V. Biomass Conversion Technologies: Fast Pyrolysis Liquids from
1235 Biomass: Quality and Upgrading, Springer, Cham; 2017, p. 55–98.
1236 doi:10.1007/978-3-319-48288-0_3.
1237 [67] Meier D, Van De Beld B, Bridgwater A V., Elliott DC, Oasmaa A, Preto F.
1238 State-of-the-art of fast pyrolysis in IEA bioenergy member countries. Renew
1239 Sustain Energy Rev 2013;20:619–41. doi:10.1016/j.rser.2012.11.061.
1240 [68] Yoder J, Galinato S, Granatstein D, Garcia-Pérez M. Economic tradeoff between
1241 biochar and bio-oil production via pyrolysis. Biomass and Bioenergy
1242 2011;35:1851–62. doi:10.1016/j.biombioe.2011.01.026.
1243 [69] Brown RC. Thermochemical processing of biomass conversion into fuels,
1244 chemicals and power. Wiley; 2011.
1245 [70] Hossain MM, Scott IM, Berruti F, Briens C. Application of Novel Pyrolysis
1246 Reactor Technology to Concentrate Bio-oil Components with Antioxidant
1247 Activity from Tobacco, Tomato and Coffee Ground Biomass. Waste and
1248 Biomass Valorization 2018;9:1607–17. doi:10.1007/s12649-017-9943-8.
1249 [71] Li D, Berruti F, Briens C. Autothermal fast pyrolysis of woody residues and
1250 wastes for the production of wood adhesives. In: M. Kuehle-Weidemeier and K.
1251 Buescher Eds., editor. Waste-to-Resources 2017, Proc. VII Int. Symp. MBT
1252 MRF, Hann. Ger., Cuvillier Verlag Gottingen; 2017, p. 215–26.
1253 [72] Tan X fei, Liu Y guo, Gu Y ling, Xu Y, Zeng G ming, Hu X jiang, et al. Biochar-
1254 based nano-composites for the decontamination of wastewater: A review.
1255 Bioresour Technol 2016;212:318–33. doi:10.1016/j.biortech.2016.04.093.

[73] Shahkarami S, Dalai AK, Soltan J. Enhanced CO2 Adsorption Using MgO-Impregnated Activated Carbon: Impact of Preparation Techniques. Ind Eng Chem Res 2016;55:5955–64. doi:10.1021/acs.iecr.5b04824.

[74] Dehkhoda AM, Gyenge E, Ellis N. A novel method to tailor the porous structure of KOH-activated biochar and its application in capacitive deionization and energy storage. Biomass and Bioenergy 2016;87:107–21. doi:10.1016/j.biombioe.2016.02.023.

[75] Briens C, Piskorz J, Berruti F. Biomass Valorization for Fuel and Chemicals Production -- A Review. Int J Chem React Eng 2008;6. doi:10.2202/1542-6580.1674.

[76] Ekström C, Lindman N, Pettersson R. Catalytic Conversion of Tars, Carbon Black and Methane from Pyrolysis/Gasification of Biomass. Fundam. Thermochem. Biomass Convers., Dordrecht: Springer Netherlands; 1985, p. 601–18. doi:10.1007/978-94-009-4932-4_34.

[77] Lira CS, Berruti FM, Palmisano P, Berruti F, Briens C, Pécora AAB. Fast pyrolysis of Amazon tucumã (Astrocaryum aculeatum) seeds in a bubbling fluidized bed reactor. J Anal Appl Pyrolysis 2013;99:23–31. doi:10.1016/j.jaap.2012.11.005.

[78] Suliman W, Harsh JB, Abu-Lail NI, Fortuna AM, Dallmeyer I, Garcia-Perez M. Modification of biochar surface by air oxidation: Role of pyrolysis temperature. Biomass and Bioenergy 2016;85:1–11. doi:10.1016/j.biombioe.2015.11.030.

[79] Zhu L, Zhao N, Tong L, Lv Y, Li G. Characterization and evaluation of surface modified materials based on porous biochar and its adsorption properties for 2,4-dichlorophenoxyacetic acid. Chemosphere 2018;210:734–44.

doi:10.1016/j.chemosphere.2018.07.090.

[80] Monlau F, Sambusiti C, Antoniou N, Barakat A, Zabaniotou A. A new concept for enhancing energy recovery from agricultural residues by coupling anaerobic digestion and pyrolysis process. Appl Energy 2015;148:32–8. doi:10.1016/j.apenergy.2015.03.024.

[81] Monlau F, Francavilla M, Sambusiti C, Antoniou N, Solhy A, Libutti A, et al. Toward a functional integration of anaerobic digestion and pyrolysis for a sustainable resource management. Comparison between solid-digestate and its derived pyrochar as soil amendment. Appl Energy 2016;169:652–62. doi:10.1016/j.apenergy.2016.02.084.

[82] Pan J, Ma J, Liu X, Zhai L, Ouyang X, Liu H. Effects of different types of biochar on the anaerobic digestion of chicken manure. Bioresour Technol 2019;275:258–65. doi:10.1016/j.biortech.2018.12.068.

[83] Wen C. Anaerobic Digestion of Aqueous Pyrolysis Condensate. Electronic Thesis and Dissertation Repository, 2018.

[84] Yang Y, Heaven S, Venetsaneas N, Banks CJ, Bridgwater A V. Slow pyrolysis of organic fraction of municipal solid waste (OFMSW): Characterisation of products and screening of the aqueous liquid product for anaerobic digestion. Appl Energy 2018;213:158–68. doi:10.1016/j.apenergy.2018.01.018.

[85] Corton J, Donnison IS, Patel M, Bühle L, Hodgson E, Wachendorf M, et al. Expanding the biomass resource: Sustainable oil production via fast pyrolysis of low input high diversity biomass and the potential integration of thermochemical and biological conversion routes. Appl Energy 2016;177:852–62. doi:10.1016/j.apenergy.2016.05.088.

1304 [86] Elsamadony M, Tawfik A, Suzuki M. Surfactant-enhanced biohydrogen
1305 production from organic fraction of municipal solid waste (OFMSW) via dry
1306 anaerobic digestion. Appl Energy 2015;149:272–82.
1307 doi:10.1016/j.apenergy.2015.03.127.
1308 [87] Monlau F, Sambusiti C, Antoniou N, Zabaniotou A, Solhy A, Barakat A.
1309 Pyrochars from bioenergy residue as novel bio-adsorbents for lignocellulosic
1310 hydrolysate detoxification. Bioresour Technol 2015;187:379–86.
1311 doi:10.1016/j.biortech.2015.03.137.
1312 [88] Erdogan E, Atila B, Mumme J, Reza MT, Toptas A, Elibol M, et al.
1313 Characterization of products from hydrothermal carbonization of orange pomace
1314 including anaerobic digestibility of process liquor. Bioresour Technol
1315 2015;196:35–42. doi:10.1016/j.biortech.2015.06.115.
1316 [89] Dufour A, Castro-Diaz M, Brosse N, Bouroukba M, Snape C. The Origin of
1317 Molecular Mobility During Biomass Pyrolysis as Revealed by In situ 1H NMR
1318 Spectroscopy. ChemSusChem 2012;5:1258–65. doi:10.1002/cssc.201100442.
1319 [90] Dufour A, Castro-Díaz M, Marchal P, Brosse N, Olcese R, Bouroukba M, et al.
1320 In Situ Analysis of Biomass Pyrolysis by High Temperature Rheology in
1321 Relations with ^{1} H NMR. Energy & Fuels 2012;26:6432–41.
1322 doi:10.1021/ef301310x.
1323 [91] Montoya J, Pecha B, Janna FC, Garcia-Perez M. Identification of the fractions
1324 responsible for morphology conservation in lignocellulosic pyrolysis:
1325 Visualization studies of sugarcane bagasse and its pseudo-components. J Anal
1326 Appl Pyrolysis 2017;123:307–18. doi:10.1016/j.jaap.2016.11.015.
1327 [92] Rangabhashiyam S, Balasubramanian P. The potential of lignocellulosic biomass

precursors for biochar production: Performance, mechanism and wastewater application—A review. Ind Crops Prod 2019;128:405–23. doi:10.1016/j.indcrop.2018.11.041.

[93] Meyer S, Glaser B, Quicker P. Technical, economical, and climate-related aspects of biochar production technologies: A literature review. Environ Sci Technol 2011;45:9473–83. doi:10.1021/es201792c.

[94] Rousset P, Aguiar C, Labbé N, Commandré JM. Enhancing the combustible properties of bamboo by torrefaction. Bioresour Technol 2011;102:8225–31. doi:10.1016/j.biortech.2011.05.093.

[95] Wilk M, Magdziarz A, Kalemba I. Characterisation of renewable fuels' torrefaction process with different instrumental techniques. Energy 2015;87:259–69. doi:10.1016/j.energy.2015.04.073.

[96] Kumar A, Saini K, Bhaskar T. Hydochar and biochar: Production, physicochemical properties and techno-economic analysis. Bioresour Technol n.d. doi:10.1016/j.biortech.2020.123442.

[97] Román S, Nabais JM V, Laginhas C, Ledesma B, González JF. Hydrothermal carbonization as an effective way of densifying the energy content of biomass. Fuel Process Technol 2012;103:78–83. doi:10.1016/j.fuproc.2011.11.009.

[98] Sabio E, Álvarez-Murillo A, Román S, Ledesma B. Conversion of tomato-peel waste into solid fuel by hydrothermal carbonization: Influence of the processing variables. Waste Manag 2016;47:122–32. doi:10.1016/j.wasman.2015.04.016.

[99] Liu Z, Zhang FS, Wu J. Characterization and application of chars produced from pinewood pyrolysis and hydrothermal treatment. Fuel 2010;89:510–4. doi:10.1016/j.fuel.2009.08.042.

[100] Hao W, Björkman E, Lilliestråle M, Hedin N. Activated carbons prepared from hydrothermally carbonized waste biomass used as adsorbents for CO2. Appl Energy 2013;112:526–32. doi:10.1016/J.APENERGY.2013.02.028.

[101] Cao X, Zhong L, Peng X, Sun S, Li S, Liu S, et al. Comparative study of the pyrolysis of lignocellulose and its major components: Characterization and overall distribution of their biochars and volatiles. Bioresour Technol 2014;155:21–7. doi:10.1016/j.biortech.2013.12.006.

[102] Tan X fei, Liu S bo, Liu Y guo, Gu Y ling, Zeng G ming, Hu X jiang, et al. Biochar as potential sustainable precursors for activated carbon production: Multiple applications in environmental protection and energy storage. Bioresour Technol 2017;227:359–72. doi:10.1016/j.biortech.2016.12.083.

[103] Cha JS, Park SH, Jung SC, Ryu C, Jeon JK, Shin MC, et al. Production and utilization of biochar: A review. J Ind Eng Chem 2016;40:1–15. doi:10.1016/j.jiec.2016.06.002.

[104] Wongrod S, Simon S, van Hullebusch ED, Lens PNL, Guibaud G. Changes of sewage sludge digestate-derived biochar properties after chemical treatments and influence on As(III and V) and Cd(II) sorption. Int Biodeterior Biodegrad 2018;135:96–102. doi:10.1016/j.ibiod.2018.10.001.

[105] Dalai AK, Azargohar R. Production of Activated Carbon from Biochar Using Chemical and Physical Activation: Mechanism and Modeling. In: Argyropoulos DS, editor. Mater. Chem. Energy from For. Biomass, American Chemical Society (ACS); 2007, p. 463–76. doi:10.1021/bk-2007-0954.ch029.

[106] You S, Ok YS, Chen SS, Tsang DCW, Kwon EE, Lee J, et al. A critical review on sustainable biochar system through gasification: Energy and environmental

applications. Bioresour Technol 2017;246:242–53. doi:10.1016/j.biortech.2017.06.177.

[107] Li H, Dong X, da Silva EB, de Oliveira LM, Chen Y, Ma LQ. Mechanisms of metal sorption by biochars: Biochar characteristics and modifications. Chemosphere 2017;178:466–78. doi:10.1016/j.chemosphere.2017.03.072.

[108] Chen Y, Zhang X, Chen W, Yang H, Chen H. The structure evolution of biochar from biomass pyrolysis and its correlation with gas pollutant adsorption performance. Bioresour Technol 2017;246:101–9. doi:10.1016/j.biortech.2017.08.138.

[109] Xie T, Reddy KR, Wang C, Yargicoglu E, Spokas K. Characteristics and applications of biochar for environmental remediation: A review. Crit Rev Environ Sci Technol 2015;45:939–69. doi:10.1080/10643389.2014.924180.

[110] Yuan Y, Bolan N, Prévoteau A, Vithanage M, Biswas JK, Ok YS, et al. Applications of biochar in redox-mediated reactions. Bioresour Technol 2017;246:271–81. doi:10.1016/j.biortech.2017.06.154.

[111] Qambrani NA, Rahman MM, Won S, Shim S, Ra C. Biochar properties and eco-friendly applications for climate change mitigation, waste management, and wastewater treatment: A review. Renew Sustain Energy Rev 2017;79:255–73. doi:10.1016/j.rser.2017.05.057.

[112] Yin Q, Zhang B, Wang R, Zhao Z. Biochar as an adsorbent for inorganic nitrogen and phosphorus removal from water: a review. Environ Sci Pollut Res 2017;24:26297–309. doi:10.1007/s11356-017-0338-y.

[113] Trigo C, Cox L, Spokas K. Influence of pyrolysis temperature and hardwood species on resulting biochar properties and their effect on azimsulfuron sorption

as compared to other sorbents. Sci Total Environ 2016;566–567:1454–64. doi:10.1016/j.scitotenv.2016.06.027.

[114] Chen T, Zhang Y, Wang H, Lu W, Zhou Z, Zhang Y, et al. Influence of pyrolysis temperature on characteristics and heavy metal adsorptive performance of biochar derived from municipal sewage sludge. Bioresour Technol 2014;164:47–54. doi:10.1016/j.biortech.2014.04.048.

[115] Collison M, Collison L, Sakrabani R, Tofield B. Biochar and Carbon Sequestration: A Regional Perspective A report prepared for East of England Development Agency (EEDA) Biochar and Carbon 2009.

[116] Antal MJ, Grønli M. The Art, Science, and Technology of Charcoal Production. Ind Eng Chem Res 2003;42:1619–1640. doi:10.1021/IE0207919.

[117] Novak JM, Busscher WJ, Laird DL, Ahmedna M, Watts DW, Niandou MAS. Impact of Biochar Amendment on Fertility of a Southeastern Coastal Plain Soil. Soil Sci 2009;174:105–12. doi:10.1097/SS.0b013e3181981d9a.

[118] Fiore S, Berruti F, Briens C. Investigation of innovative and conventional pyrolysis of ligneous and herbaceous biomasses for biochar production. Biomass and Bioenergy 2018.

[119] Suliman W, Harsh JB, Abu-Lail NI, Fortuna AM, Dallmeyer I, Garcia-Perez M. Influence of feedstock source and pyrolysis temperature on biochar bulk and surface properties. Biomass and Bioenergy 2016;84:37–48. doi:10.1016/j.biombioe.2015.11.010.

[120] Tan Z, Lin CSK, Ji X, Rainey TJ. Returning biochar to fields: A review. Appl Soil Ecol 2017;116:1–11. doi:10.1016/j.apsoil.2017.03.017.

[121] Ahmed MB, Zhou JL, Ngo HH, Guo W. Insight into biochar properties and its

cost analysis. Biomass and Bioenergy 2016;84:76–86. doi:10.1016/j.biombioe.2015.11.002.

[122] Nguyen BT, Lehmann J. Black carbon decomposition under varying water regimes. Org Geochem 2009;40:846–53. doi:10.1016/j.orggeochem.2009.05.004.

[123] Klüpfel L, Keiluweit M, Kleber M, Sander M. Redox Properties of Plant Biomass-Derived Black Carbon (Biochar). Environ Sci Technol 2014;48:5601–11. doi:10.1021/es500906d.

[124] Singh, Balwant, Camps-Arbestain M, Lehmann J, (Eds). Biochar: a guide to analytical methods. CSIRO Publishing; 2017.

[125] Appels L, Baeyens J, Degrève J, Dewil R. Principles and potential of the anaerobic digestion of waste-activated sludge. Prog Energy Combust Sci 2008;34:755–81. doi:10.1016/j.pecs.2008.06.002.

[126] Zhang C, Su H, Baeyens J, Tan T. Reviewing the anaerobic digestion of food waste for biogas production. Renew Sustain Energy Rev 2014;38:383–92. doi:10.1016/J.RSER.2014.05.038.

[127] Ren Y, Yu M, Wu C, Wang Q, Gao M, Huang Q, et al. A comprehensive review on food waste anaerobic digestion: Research updates and tendencies. Bioresour Technol 2018;247:1069–76. doi:10.1016/J.BIORTECH.2017.09.109.

[128] Di Maria F, Sordi A, Cirulli G, Micale C. Amount of energy recoverable from an existing sludge digester with the co-digestion with fruit and vegetable waste at reduced retention time. Appl Energy 2015;150:9–14. doi:10.1016/j.apenergy.2015.01.146.

[129] Elalami D, Carrere H, Monlau F, Abdelouahdi K, Oukarroum A, Barakat A. Pretreatment and co-digestion of wastewater sludge for biogas production:

Recent research advances and trends. Renew Sustain Energy Rev 2019;114:109287. doi:10.1016/j.rser.2019.109287.

[130] Nghiem LD, Koch K, Bolzonella D, Drewes JE. Full scale co-digestion of wastewater sludge and food waste: Bottlenecks and possibilities. Renew Sustain Energy Rev 2017;72:354–62. doi:10.1016/j.rser.2017.01.062.

[131] Kang X, Sun Y, Li L, Kong X, Yuan Z. Improving methane production from anaerobic digestion of Pennisetum Hybrid by alkaline pretreatment. Bioresour Technol 2018;255:205–12. doi:10.1016/j.biortech.2017.12.001.

[132] Novais RM, Gameiro T, Carvalheiras J, Seabra MP, Tarelho LAC, Labrincha JA, et al. High pH buffer capacity biomass fly ash-based geopolymer spheres to boost methane yield in anaerobic digestion. J Clean Prod 2018;178:258–67. doi:10.1016/j.jclepro.2018.01.033.

[133] Novais RM, Buruberri LH, Seabra MP, Bajare D, Labrincha JA. Novel porous fly ash-containing geopolymers for pH buffering applications. J Clean Prod 2016;124:395–404. doi:10.1016/j.jclepro.2016.02.114.

[134] Wei W, Guo W, Ngo HH, Mannina G, Wang D, Chen X, et al. Enhanced high-quality biomethane production from anaerobic digestion of primary sludge by corn stover biochar. Bioresour Technol 2020;306:123159. doi:10.1016/j.biortech.2020.123159.

[135] Ambaye TG, Rene ER, Dupont C, Wongrod S, van Hullebusch ED. Anaerobic Digestion of Fruit Waste Mixed With Sewage Sludge Digestate Biochar: Influence on Biomethane Production. Front Energy Res 2020;8:31. doi:10.3389/fenrg.2020.00031.

[136] Qiang H, Lang DL, Li YY. High-solid mesophilic methane fermentation of food

1472 waste with an emphasis on Iron, Cobalt, and Nickel requirements. Bioresour
1473 Technol 2012;103:21–7. doi:10.1016/j.biortech.2011.09.036.
1474 [137] Chen Y, Cheng JJ, Creamer KS. Inhibition of anaerobic digestion process: A
1475 review. Bioresour Technol 2008;99:4044–64.
1476 doi:10.1016/j.biortech.2007.01.057.
1477 [138] Wang G, Li Q, Li Y, Xing Y, Yao G, Liu Y, et al. Redox-active biochar
1478 facilitates potential electron tranfer between syntrophic partners to enhance
1479 anaerobic digestion under high organic loading rate. Bioresour Technol
1480 2020;298:122524. doi:10.1016/j.biortech.2019.122524.
1481 [139] Qin Y, Wang H, Li X, Cheng JJ, Wu W. Improving methane yield from organic
1482 fraction of municipal solid waste (OFMSW) with magnetic rice-straw biochar.
1483 Bioresour Technol 2017;245:1058–66. doi:10.1016/j.biortech.2017.09.047.
1484 [140] Rajagopal R, Massé DI, Singh G. A critical review on inhibition of anaerobic
1485 digestion process by excess ammonia. Bioresour Technol 2013;143:632–41.
1486 doi:10.1016/j.biortech.2013.06.030.
1487 [141] Zhang Y, Zamudio Cañas EM, Zhu Z, Linville JL, Chen S, He Q. Robustness of
1488 archaeal populations in anaerobic co-digestion of dairy and poultry wastes.
1489 Bioresour Technol 2011;102:779–85. doi:10.1016/j.biortech.2010.08.104.
1490 [142] Ho L, Ho G. Mitigating ammonia inhibition of thermophilic anaerobic treatment
1491 of digested piggery wastewater: Use of pH reduction, zeolite, biomass and humic
1492 acid. Water Res 2012;46:4339–50. doi:10.1016/j.watres.2012.05.016.
1493 [143] Poirier S, Madigou C, Bouchez T, Chapleur O. Improving anaerobic digestion
1494 with support media: Mitigation of ammonia inhibition and effect on microbial
1495 communities. Bioresour Technol 2017;235:229–39.

1496 doi:10.1016/j.biortech.2017.03.099.
1497 [144] Yenigün O, Demirel B. Ammonia inhibition in anaerobic digestion: A review.
1498 Process Biochem 2013;48:901–11. doi:10.1016/j.procbio.2013.04.012.
1499 [145] Yun YM, Kim DH, Cho SK, Shin HS, Jung KW, Kim HW. Mitigation of
1500 ammonia inhibition by internal dilution in high-rate anaerobic digestion of food
1501 waste leachate and evidences of microbial community response. Biotechnol
1502 Bioeng 2016;113:1892–901. doi:10.1002/bit.25968.
1503 [146] Fang C, Boe K, Angelidaki I. Anaerobic co-digestion of desugared molasses with
1504 cow manure; focusing on sodium and potassium inhibition. Bioresour Technol
1505 2011;102:1005–11. doi:10.1016/j.biortech.2010.09.077.
1506 [147] Wang Q, Yang Y, Yu C, Huang H, Kim M, Feng C, et al. Study on a fixed
1507 zeolite bioreactor for anaerobic digestion of ammonium-rich swine wastes.
1508 Bioresour Technol 2011;102:7064–8. doi:10.1016/j.biortech.2011.04.085.
1509 [148] Wang W, Ren X, Yang K, Hu Z, Yuan S. Inhibition of ammonia on anaerobic
1510 digestion of synthetic coal gasification wastewater and recovery using struvite
1511 precipitation. J Hazard Mater 2017;340:152–9.
1512 doi:10.1016/j.jhazmat.2017.07.002.
1513 [149] Zhang Y, Angelidaki I. Counteracting ammonia inhibition during anaerobic
1514 digestion by recovery using submersible microbial desalination cell. Biotechnol
1515 Bioeng 2015;112:1478–82. doi:10.1002/bit.25549.
1516 [150] Ghyselbrecht K, Monballiu A, Somers MH, Sigurnjak I, Meers E, Appels L, et
1517 al. Stripping and scrubbing of ammonium using common fractionating columns
1518 to prove ammonium inhibition during anaerobic digestion. Int J Energy Environ
1519 Eng 2018;9:447–55. doi:10.1007/s40095-018-0283-7.

[151] Shen Y, Linville JL, Urgun-Demirtas M, Schoene RP, Snyder SW. Producing pipeline-quality biomethane via anaerobic digestion of sludge amended with corn stover biochar with in-situ CO2 removal. Appl Energy 2015;158:300–9. doi:10.1016/j.apenergy.2015.08.016.

[152] Ciccoli R, Sperandei M, Petrazzuolo F, Broglia M, Chiarini L, Correnti A, et al. Anaerobic digestion of the above ground biomass of Jerusalem Artichoke in a pilot plant: Impact of the preservation method on the biogas yield and microbial community. Biomass and Bioenergy 2018;108:190–7. doi:10.1016/j.biombioe.2017.11.003.

[153] Lü F, Hua Z, Shao L, He P. Loop bioenergy production and carbon sequestration of polymeric waste by integrating biochemical and thermochemical conversion processes: A conceptual framework and recent advances. Renew Energy 2018;124:202–11. doi:10.1016/j.renene.2017.10.084.

[154] Takaya CA, Fletcher LA, Singh S, Anyikude KU, Ross AB. Phosphate and ammonium sorption capacity of biochar and hydrochar from different wastes. Chemosphere 2016;145:518–27. doi:10.1016/j.chemosphere.2015.11.052.

[155] Kizito S, Wu S, Kirui WK, Lei M, Lu Q, Bah H, et al. Evaluation of slow pyrolyzed wood and rice husks biochar for adsorption of ammonium nitrogen from piggery manure anaerobic digestate slurry. Sci Total Environ 2015;505:102–12. doi:10.1016/j.scitotenv.2014.09.096.

[156] Wang Z, Guo H, Shen F, Yang G, Zhang Y, Zeng Y, et al. Biochar produced from oak sawdust by Lanthanum (La)-involved pyrolysis for adsorption of ammonium (NH4+), nitrate (NO3-), and phosphate (PO43-). Chemosphere 2015;119:646–53. doi:10.1016/j.chemosphere.2014.07.084.

[157] Zeng Z, Zhang S, Li T, Zhao F, He Z, Zhao H, et al. Sorption of ammonium and phosphate from aqueous solution by biochar derived from phytoremediation plants. J Zhejiang Univ Sci B 2013;14:1152–61. doi:10.1631/jzus.B1300102.

[158] Zhang Y, Li Z, Mahmood IB. Recovery of NH4+by corn cob produced biochars and its potential application as soil conditioner. Front Environ Sci Eng 2014;8:825–34. doi:10.1007/s11783-014-0682-9.

[159] Kizito S, Wu S, Wandera SM, Guo L, Dong R. Evaluation of ammonium adsorption in biochar-fixed beds for treatment of anaerobically digested swine slurry: Experimental optimization and modeling. Sci Total Environ 2016;563–564:1095–104. doi:10.1016/j.scitotenv.2016.05.149.

[160] Lopez RJ, Higgins SR, Pagaling E, Yan T, Cooney MJ. High rate anaerobic digestion of wastewater separated from grease trap waste. Renew Energy 2014;62:234–42. doi:10.1016/j.renene.2013.06.047.

[161] Lettinga G. Anaerobic digestion and wastewater treatment systems. Antonie Van Leeuwenhoek 1995;67:3–28. doi:10.1007/BF00872193.

[162] Laine J, Simoni S, Calles R. Preparation of activated carbon from coconut shell in a a small scale cocurrent flow rotary kiln. Chem Eng Commun 1991;99:15–23. doi:10.1080/00986449108911575.

[163] Watanabe Y, Tanaka K. Innovative sludge handling through pelletization/thickening. Water Res 1999;33:3245–52. doi:10.1016/S0043-1354(99)00045-7.

[164] Sawayama S, Tada C, Tsukahara K, Yagishita T. Effect of ammonium addition on methanogenic community in a fluidized bed anaerobic digestion. J Biosci Bioeng 2004;97:65–70. doi:10.1016/S1389-1723(04)70167-X.

[165] Stams AJM. Metabolic interactions between anaerobic bacteria in methanogenic environments. Antonie Van Leeuwenhoek 1994;66:271–94. doi:10.1007/BF00871644.

[166] Whitman WB, Bowen TL, Boone DR. The Methanogenic Bacteria. The Prokaryotes, New York, NY: Springer New York; 2006, p. 165–207. doi:10.1007/0-387-30743-5_9.

[167] Morris BEL, Henneberger R, Huber H, Moissl-Eichinger C. Microbial syntrophy: Interaction for the common good. FEMS Microbiol Rev 2013;37:384–406. doi:10.1111/1574-6976.12019.

[168] Schink B, Montag D, Keller A, Müller N. Hydrogen or formate: Alternative key players in methanogenic degradation. Environ Microbiol Rep 2017;9:189–202. doi:10.1111/1758-2229.12524.

[169] Lovley DR, Fraga JL, Coates JD, Blunt-Harris EL. Humics as an electron donor for anaerobic respiration. Environ Microbiol 1999;1:89–98. doi:10.1046/j.1462-2920.1999.00009.x.

[170] Roden EE, Kappler A, Bauer I, Jiang J, Paul A, Stoesser R, et al. Extracellular electron transfer through microbial reduction of solid-phase humic substances. Nat Geosci 2010;3:417–21. doi:10.1038/ngeo870.

[171] Park JH, Kang HJ, Park KH, Park HD. Direct interspecies electron transfer via conductive materials: A perspective for anaerobic digestion applications. Bioresour Technol 2018;254:300–11. doi:10.1016/j.biortech.2018.01.095.

[172] McGlynn SE, Chadwick GL, Kempes CP, Orphan VJ. Single cell activity reveals direct electron transfer in methanotrophic consortia. Nature 2015;526:531–5. doi:10.1038/nature15512.

[173] Lovley DR. Happy together: microbial communities that hook up to swap electrons. ISME J 2017;11:327–36. doi:10.1038/ismej.2016.136.

[174] Stams AJM, Plugge CM. Electron transfer in syntrophic communities of anaerobic bacteria and archaea. Nat Rev Microbiol 2009;7:568–77. doi:10.1038/nrmicro2166.

[175] Schink B, Thauer R. Energetics of syntrophic methane formation and the influence of aggregation. In: Lettinga G, Zehnder, A.J.B. Grotenhuis,J.T.C. Hulshoff LW, editors. Granul. Anaerob. sludge; Microbiol. Technol. Proc. GASMAT - Work. Lunteren, Netherlands, 25-27 Oct. 1987 , Centre for Agricultural Publishing and Documentation; 1988, p. 5–17.

[176] Summers ZM, Fogarty HE, Leang C, Franks AE, Malvankar NS, Lovley DR. Direct Exchange of Electrons Within Aggregates of an Evolved Syntrophic Coculture of Anaerobic Bacteria. Science (80-) 2010;330:1413–5. doi:10.1126/science.1196526.

[177] Rotaru AE, Shrestha PM, Liu F, Shrestha M, Shrestha D, Embree M, et al. A new model for electron flow during anaerobic digestion: Direct interspecies electron transfer to Methanosaeta for the reduction of carbon dioxide to methane. Energy Environ Sci 2014;7:408–15. doi:10.1039/c3ee42189a.

[178] Rotaru A-E, Shrestha PM, Liu F, Markovaite B, Chen S, Nevin KP, et al. Direct interspecies electron transfer between Geobacter metallireducens and Methanosarcina barkeri. Appl Environ Microbiol 2014;80:4599–605. doi:10.1128/AEM.00895-14.

[179] Liu F, Rotaru A-E, Shrestha PM, Malvankar NS, Nevin KP, Lovley DR. Magnetite compensates for the lack of a pilin-associated *c* -type cytochrome in

extracellular electron exchange. Environ Microbiol 2015;17:648–55. doi:10.1111/1462-2920.12485.

[180] Liu F, Rotaru A-E, Shrestha PM, Malvankar NS, Nevin KP, Lovley DR. Promoting direct interspecies electron transfer with activated carbon. Energy Environ Sci 2012;5:8982. doi:10.1039/c2ee22459c.

[181] Barua S, Dhar BR. Advances towards understanding and engineering direct interspecies electron transfer in anaerobic digestion. Bioresour Technol 2017;244:698–707. doi:10.1016/j.biortech.2017.08.023.

[182] Cheah S, Malone SC, Feik CJ. Speciation of Sulfur in Biochar Produced from Pyrolysis and Gasification of Oak and Corn Stover. Environ Sci Technol 2014;48:8474–80. doi:10.1021/es500073r.

[183] Rosas JG, Gómez N, Cara J, Ubalde J, Sort X, Sánchez ME. Assessment of sustainable biochar production for carbon abatement from vineyard residues. J Anal Appl Pyrolysis 2015;113:239–47. doi:10.1016/J.JAAP.2015.01.011.

[184] Coelho JJ, Prieto ML, Dowling S, Hennessy A, Casey I, Woodcock T, et al. Physical-chemical traits, phytotoxicity and pathogen detection in liquid anaerobic digestates. Waste Manag 2018;78:8–15. doi:10.1016/j.wasman.2018.05.017.

[185] Di Maria F, Sordi A, Cirulli G, Gigliotti G, Massaccesi L, Cucina M. Co-treatment of fruit and vegetable waste in sludge digesters. An analysis of the relationship among bio-methane generation, process stability and digestate phytotoxicity. Waste Manag 2014;34:1603–8. doi:10.1016/j.wasman.2014.05.017.

[186] Di Maria F, Gigliotti G, Sordi A, Micale C, Zadra C, Massaccesi L. Hybrid solid anaerobic digestion batch: biomethane production and mass recovery from the

organic fraction of solid waste. Waste Manag Res 2013;31:869–73. doi:10.1177/0734242X13477902.

[187] Moukazis I, Pellera FM, Gidarakos E. Slaughterhouse by-products treatment using anaerobic digestion. Waste Manag 2018;71:652–62. doi:10.1016/j.wasman.2017.07.009.

[188] Fuchs W, Drosg B. Assessment of the state of the art of technologies for the processing of digestate residue from anaerobic digesters. Water Sci Technol 2013;67:1984–93. doi:10.2166/wst.2013.075.

[189] Vaneeckhaute C, Lebuf V, Michels E, Belia E, Vanrolleghem PA, Tack FMG, et al. Nutrient Recovery from Digestate: Systematic Technology Review and Product Classification. Waste and Biomass Valorization 2017;8:21–40. doi:10.1007/s12649-016-9642-x.

[190] Egle L, Rechberger H, Zessner M. Overview and description of technologies for recovering phosphorus from municipal wastewater. Resour Conserv Recycl 2015;105:325–46. doi:10.1016/j.resconrec.2015.09.016.

[191] Dahlin J, Nelles M, Herbes C. Biogas digestate management: Evaluating the attitudes and perceptions of German gardeners towards digestate-based soil amendments. Resour Conserv Recycl 2017;118:27–38. doi:10.1016/j.resconrec.2016.11.020.

[192] Bagreev A, Bandosz TJ, Locke DC. Pore structure and surface chemistry of adsorbents obtained by pyrolysis of sewage sludge-derived fertilizer. Carbon N Y 2001;39:1971–9. doi:10.1016/S0008-6223(01)00026-4.

[193] Jiang B, Lin Y, Mbog JC. Biochar derived from swine manure digestate and applied on the removals of heavy metals and antibiotics. Bioresour Technol

2018;270:603–11. doi:10.1016/j.biortech.2018.08.022.

[194] Li J, Zhang M, Ye Z, Yang C. Effect of manganese oxide-modified biochar addition on methane production and heavy metal speciation during the anaerobic digestion of sewage sludge. J Environ Sci 2019;76:267–77. doi:10.1016/j.jes.2018.05.009.

[195] Zhang L, Li F, Kuroki A, Loh KC, Wang CH, Dai Y, et al. Methane yield enhancement of mesophilic and thermophilic anaerobic co-digestion of algal biomass and food waste using algal biochar: Semi-continuous operation and microbial community analysis. Bioresour Technol 2020;302:122892. doi:10.1016/j.biortech.2020.122892.

[196] Martin SL, Clarke ML, Othman M, Ramsden SJ, West HM. Biochar-mediated reductions in greenhouse gas emissions from soil amended with anaerobic digestates. Biomass and Bioenergy 2014;79:39–49. doi:10.1016/j.biombioe.2015.04.030.

[197] Marchetti R, Castelli F. Biochar from Swine Solids and Digestate Influence Nutrient Dynamics and Carbon Dioxide Release in Soil. J Environ Qual 2013;42:893–901. doi:10.2134/jeq2012.0352.

[198] Mukherjee S, Weihermueller L, Tappe W, Vereecken H, Burauel P. Microbial respiration of biochar- and digestate-based mixtures. Biol Fertil Soils 2016;52:151–64. doi:10.1007/s00374-015-1060-x.

[199] Cardelli R, Giussani G, Marchini F, Saviozzi A. Short-term effects on soil of biogas digestate, biochar and their combinations. Soil Res 2018;56:623. doi:10.1071/SR18017.

[200] Vaughn SF, Eller FJ, Evangelista RL, Moser BR, Lee E, Wagner RE, et al.

Evaluation of biochar-anaerobic potato digestate mixtures as renewable components of horticultural potting media. Ind Crops Prod 2015;65:467–71. doi:10.1016/j.indcrop.2014.10.040.

[201] Zhang J, Lü F, Shao L, He P. The use of biochar-amended composting to improve the humification and degradation of sewage sludge. Bioresour Technol 2014;168:252–8. doi:10.1016/j.biortech.2014.02.080.

[202] Bustamante MA, Alburquerque JA, Restrepo AP, de la Fuente C, Paredes C, Moral R, et al. Co-composting of the solid fraction of anaerobic digestates, to obtain added-value materials for use in agriculture. Biomass and Bioenergy 2012;43:26–35. doi:10.1016/j.biombioe.2012.04.010.

[203] Godlewska P, Schmidt HP, Ok YS, Oleszczuk P. Biochar for composting improvement and contaminants reduction. A review. Bioresour Technol 2017;246:193–202. doi:10.1016/j.biortech.2017.07.095.

[204] Xiao R, Awasthi MK, Li R, Park J, Pensky SM, Wang Q, et al. Recent developments in biochar utilization as an additive in organic solid waste composting: A review. Bioresour Technol 2017;246:203–13. doi:10.1016/j.biortech.2017.07.090.

[205] Sanchez-Monedero MA, Cayuela ML, Roig A, Jindo K, Mondini C, Bolan N. Role of biochar as an additive in organic waste composting. Bioresour Technol 2018;247:1155–64. doi:10.1016/j.biortech.2017.09.193.

[206] Cristina G, Camelin E, Pugliese M, Tommasi T, Fino D. Evaluation of anaerobic digestates from sewage sludge as a potential solution for improvement of soil fertility. Waste Manag 2019;99:122–34. doi:10.1016/j.wasman.2019.08.018.

[207] Angelidaki I, Treu L, Tsapekos P, Luo G, Campanaro S, Wenzel H, et al. Biogas

upgrading and utilization: Current status and perspectives. Biotechnol Adv 2018;36:452–66. doi:10.1016/J.BIOTECHADV.2018.01.011.

[208] Browne J, Nizami A-S, Thamsiriroj T, Murphy JD. Assessing the cost of biofuel production with increasing penetration of the transport fuel market: A case study of gaseous biomethane in Ireland. Renew Sustain Energy Rev 2011;15:4537–47. doi:10.1016/J.RSER.2011.07.098.

[209] Petersson A, WeLLInGer A. Biogas upgrading technologies–developments and innovations. IEA Bioenergy 2009;20:1–19.

[210] Sun Q, Li H, Yan J, Liu L, Yu Z, Yu X. Selection of appropriate biogas upgrading technology-a review of biogas cleaning, upgrading and utilisation. Renew Sustain Energy Rev 2015;51:521–32. doi:10.1016/J.RSER.2015.06.029.

[211] Miltner M, Makaruk A, Harasek M. Review on available biogas upgrading technologies and innovations towards advanced solutions. J Clean Prod 2017;161:1329–37. doi:10.1016/J.JCLEPRO.2017.06.045.

[212] Singh G, Lakhi KS, Sil S, Bhosale S V., Kim IY, Albahily K, et al. Biomass derived porous carbon for CO 2 capture. Carbon N Y 2019;148:164–86. doi:10.1016/j.carbon.2019.03.050.

[213] Ahmed R, Liu G, Yousaf B, Abbas Q, Ullah H, Ali MU. Recent advances in carbon-based renewable adsorbent for selective carbon dioxide capture and separation-A review. J Clean Prod 2020;242:118409. doi:10.1016/j.jclepro.2019.118409.

[214] Dissanayake PD, You S, Igalavithana AD, Xia Y, Bhatnagar A, Gupta S, et al. Biochar-based adsorbents for carbon dioxide capture: A critical review. Renew Sustain Energy Rev 2020;119:109582. doi:10.1016/j.rser.2019.109582.

1736 [215] Sethupathi S, Zhang M, Rajapaksha A, Lee S, Mohamad Nor N, Mohamed A, et
1737 al. Biochars as Potential Adsorbers of CH4, CO2 and H2S. Sustainability
1738 2017;9:121. doi:10.3390/su9010121.
1739 [216] Creamer AE, Gao B, Zhang M. Carbon dioxide capture using biochar produced
1740 from sugarcane bagasse and hickory wood. Chem Eng J 2014;249:174–9.
1741 doi:10.1016/J.CEJ.2014.03.105.
1742 [217] Creamer AE, Gao B. Carbon-Based Adsorbents for Postcombustion CO2
1743 Capture: A Critical Review. Environ Sci Technol 2016;50:7276–89.
1744 doi:10.1021/acs.est.6b00627.
1745 [218] Presser V, McDonough J, Yeon S-H, Gogotsi Y. Effect of pore size on carbon
1746 dioxide sorption by carbide derived carbon. Energy Environ Sci 2011;4:3059.
1747 doi:10.1039/c1ee01176f.
1748 [219] Xu X, Kan Y, Zhao L, Cao X. Chemical transformation of CO2 during its
1749 capture by waste biomass derived biochars. Environ Pollut 2016;213:533–40.
1750 doi:10.1016/j.envpol.2016.03.013.
1751 [220] Jung S, Park YK, Kwon EE. Strategic use of biochar for CO2 capture and
1752 sequestration. J CO2 Util 2019;32:128–39. doi:10.1016/j.jcou.2019.04.012.
1753 [221] Sahota S, Vijay VK, Subbarao PMV, Chandra R, Ghosh P, Shah G, et al.
1754 Characterization of leaf waste based biochar for cost effective hydrogen sulphide
1755 removal from biogas. Bioresour Technol 2018;250:635–41.
1756 doi:10.1016/J.BIORTECH.2017.11.093.
1757 [222] Kanjanarong J, Giri BS, Jaisi DP, Oliveira FR, Boonsawang P, Chaiprapat S, et
1758 al. Removal of hydrogen sulfide generated during anaerobic treatment of sulfate-
1759 laden wastewater using biochar: Evaluation of efficiency and mechanisms.

1760 Bioresour Technol 2017;234:115–21. doi:10.1016/J.BIORTECH.2017.03.009.
1761 [223] Bamdad H, Hawboldt K, MacQuarrie S. A review on common adsorbents for
1762 acid gases removal: Focus on biochar. Renew Sustain Energy Rev
1763 2018;81:1705–20. doi:10.1016/J.RSER.2017.05.261.
1764 [224] Sun Y, Zhang JP, Wen C, Zhang L. An enhanced approach for biochar
1765 preparation using fluidized bed and its application for H2S removal. Chem Eng
1766 Process Process Intensif 2016;104:1–12. doi:10.1016/j.cep.2016.02.006.
1767 [225] Xu X, Cao X, Zhao L, Sun T. Comparison of sewage sludge- and pig manure-
1768 derived biochars for hydrogen sulfide removal. Chemosphere 2014;111:296–303.
1769 doi:10.1016/j.chemosphere.2014.04.014.
1770 [226] Sun Y, Yang G, Zhang L, Sun Z. Preparation of high performance H2S removal
1771 biochar by direct fluidized bed carbonization using potato peel waste. Process Saf
1772 Environ Prot 2017;107:281–8. doi:10.1016/j.psep.2017.02.018.
1773 [227] Shang G, Shen G, Liu L, Chen Q, Xu Z. Kinetics and mechanisms of hydrogen
1774 sulfide adsorption by biochars. Bioresour Technol 2013;133:495–9.
1775 doi:10.1016/j.biortech.2013.01.114.
1776 [228] Madzaki H, Karimghani WAWAB, Nurzalikharebitanim, Azilbaharialias.
1777 Carbon Dioxide Adsorption on Sawdust Biochar. Procedia Eng 2016;148:718–
1778 25. doi:10.1016/j.proeng.2016.06.591.
1779 [229] Shahkarami S, Azargohar R, Dalai AK, Soltan J. Breakthrough CO2 adsorption
1780 in bio-based activated carbons. J Environ Sci (China) 2015;34:68–76.
1781 doi:10.1016/j.jes.2015.03.008.
1782 [230] Lahijani P, Mohammadi M, Mohamed AR. Metal incorporated biochar as a
1783 potential adsorbent for high capacity CO2 capture at ambient condition. J CO2

1784 Util 2018;26:281–93. doi:10.1016/j.jcou.2018.05.018.
1785 [231] Guedes RE, Luna AS, Torres AR. Operating parameters for bio-oil production in
1786 biomass pyrolysis: A review. J Anal Appl Pyrolysis 2018;129:134–49.
1787 doi:10.1016/j.jaap.2017.11.019.
1788 [232] Li W, Dang Q, Brown RC, Laird D, Wright MM. The impacts of biomass
1789 properties on pyrolysis yields, economic and environmental performance of the
1790 pyrolysis-bioenergy-biochar platform to carbon negative energy. Bioresour
1791 Technol 2017;241:959–68. doi:10.1016/j.biortech.2017.06.049.
1792 [233] Ji C, Cheng K, Nayak D, Pan G. Environmental and economic assessment of
1793 crop residue competitive utilization for biochar, briquette fuel and combined heat
1794 and power generation. J Clean Prod 2018;192:916–23.
1795 doi:10.1016/j.jclepro.2018.05.026.
1796 [234] Harsono SS, Grundman P, Lau LH, Hansen A, Salleh MAM, Meyer-Aurich A, et
1797 al. Energy balances, greenhouse gas emissions and economics of biochar
1798 production from palm oil empty fruit bunches. Resour Conserv Recycl
1799 2013;77:108–15. doi:10.1016/j.resconrec.2013.04.005.
1800 [235] Sahoo K, Bilek E, Bergman R, Mani S. Techno-economic analysis of producing
1801 solid biofuels and biochar from forest residues using portable systems. Appl
1802 Energy 2019;235:578–90. doi:10.1016/J.APENERGY.2018.10.076.
1803 [236] ICIS. Analytics - ICIS Explore 2018.
1804 https://www.icis.com/explore/services/analytics/?intcmp=mega-menu-explore-
1805 services-analytics&redirect=english (accessed January 2, 2019).
1806 [237] Menya E, Olupot PW, Storz H, Lubwama M, Kiros Y. Production and
1807 performance of activated carbon from rice husks for removal of natural organic

matter from water: A review. Chem Eng Res Des 2018;129:271–96. doi:10.1016/j.cherd.2017.11.008.

[238] Shabangu S, Woolf D, Fisher EM, Angenent LT, Lehmann J. Techno-economic assessment of biomass slow pyrolysis into different biochar and methanol concepts. Fuel 2014;117:742–8. doi:10.1016/j.fuel.2013.08.053.

[239] Dickinson D, Balduccio L, Buysse J, Ronsse F, van Huylenbroeck G, Prins W. Cost-benefit analysis of using biochar to improve cereals agriculture. GCB Bioenergy 2015;7:850–64. doi:10.1111/gcbb.12180.

[240] Jirka S, Tomlinson T. State of the biochar industry 2014. A survey of commercial activity in the biochar field. 2015.

[241] Jirka S, Tomlinson T. 2013 State of the biochar industry. A Survey of commercial activity in the biochar field. 2014.

[242] Antoniou N, Monlau F, Sambusiti C, Ficara E, Barakat A, Zabaniotou A. Contribution to Circular Economy options of mixed agricultural wastes management: Coupling anaerobic digestion with gasification for enhanced energy and material recovery. J Clean Prod 2019;209:505–14. doi:10.1016/j.jclepro.2018.10.055.

[243] Zhang L, Lim EY, Loh KC, Ok YS, Lee JTE, Shen Y, et al. Biochar enhanced thermophilic anaerobic digestion of food waste: Focusing on biochar particle size, microbial community analysis and pilot-scale application. Energy Convers Manag 2020;209:112654. doi:10.1016/j.enconman.2020.112654.

[244] Sharifzadeh M, Sadeqzadeh M, Guo M, Borhani TN, Murthy Konda NVSN, Garcia MC, et al. The multi-scale challenges of biomass fast pyrolysis and bio-oil upgrading: Review of the state of art and future research directions. Prog Energy

1832 Combust Sci 2019;71:1–80. doi:10.1016/J.PECS.2018.10.006.
1833 [245] GREET. GREET Models 2018. https://greet.es.anl.gov/greet.models (accessed
1834 January 2, 2019).
1835 [246] EPA U. Overview for Renewable Fuel Standard 2017.
1836 [247] Moreira MT, Noya I, Feijoo G. The prospective use of biochar as adsorption
1837 matrix – A review from a lifecycle perspective. Bioresour Technol
1838 2017;246:135–41. doi:10.1016/j.biortech.2017.08.041.
1839 [248] Mohan D, Sarswat A, Ok YS, Pittman CU. Organic and inorganic contaminants
1840 removal from water with biochar, a renewable, low cost and sustainable
1841 adsorbent - A critical review. Bioresour Technol 2014;160:191–202.
1842 doi:10.1016/j.biortech.2014.01.120.
1843 [249] Ibarrola R, Shackley S, Hammond J. Pyrolysis biochar systems for recovering
1844 biodegradable materials: A life cycle carbon assessment. Waste Manag
1845 2012;32:859–68. doi:10.1016/j.wasman.2011.10.005.
1846 [250] Pratt K, Moran D. Evaluating the cost-effectiveness of global biochar mitigation
1847 potential. Biomass and Bioenergy 2010;34:1149–58.
1848 doi:10.1016/j.biombioe.2010.03.004.
1849 [251] Nowrouzi M, Younesi H, Bahramifar N. High efficient carbon dioxide capture
1850 onto as-synthesized activated carbon by chemical activation of Persian Ironwood
1851 biomass and the economic pre-feasibility study for scale-up. J Clean Prod
1852 2017;168:499–509. doi:10.1016/j.jclepro.2017.09.080.
1853 [252] Muñoz E, Curaqueo G, Cea M, Vera L, Navia R. Environmental hotspots in the
1854 life cycle of a biochar-soil system. J Clean Prod 2017;158:1–7.
1855 doi:10.1016/j.jclepro.2017.04.163.

[253] Hammond J, Shackley S, Sohi S, Brownsort P. Prospective life cycle carbon abatement for pyrolysis biochar systems in the UK. Energy Policy 2011;39:2646–55. doi:10.1016/j.enpol.2011.02.033.

[254] Brassard P, Godbout S, Pelletier F, Raghavan V, Palacios JH. Biomass and Bioenergy Pyrolysis of switchgrass in an auger reactor for biochar production : A greenhouse gas and energy impacts assessment. Biomass and Bioenergy 2018;116:99–105. doi:10.1016/j.biombioe.2018.06.007.

[255] Righi S, Bandini V, Marazza D, Baioli F, Torri C, Contin A. Life Cycle Assessment of high ligno-cellulosic biomass pyrolysis coupled with anaerobic digestion. Bioresour Technol 2016;212:245–53. doi:10.1016/j.biortech.2016.04.052.

[256] Matuštík J, Hnátková T, Kočí V. Life cycle assessment of biochar-to-soil systems: A review. J Clean Prod 2020;259. doi:10.1016/j.jclepro.2020.120998.

[257] Hjaila K, Baccar R, Sarrà M, Gasol CM, Blánquez P. Environmental impact associated with activated carbon preparation from olive-waste cake via life cycle assessment. J Environ Manage 2013;130:242–7. doi:10.1016/j.jenvman.2013.08.061.

[258] Kookana RS, Sarmah AK, Van Zwieten L, Krull E, Singh B. Biochar application to soil. agronomic and environmental benefits and unintended consequences. vol. 112. 1st ed. Elsevier Inc.; 2011. doi:10.1016/B978-0-12-385538-1.00003-2.

[259] Li H, Feng K. Life cycle assessment of the environmental impacts and energy efficiency of an integration of sludge anaerobic digestion and pyrolysis. J Clean Prod 2018;195:476–85. doi:10.1016/J.JCLEPRO.2018.05.259.